### Catania, 12–14 settembre 2018

# **ABSTRACT BOOK**

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PETROLOG

# Congresso congiunto SGI-SIMP



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«Geosciences for the environment, natural hazards and cultural heritage»

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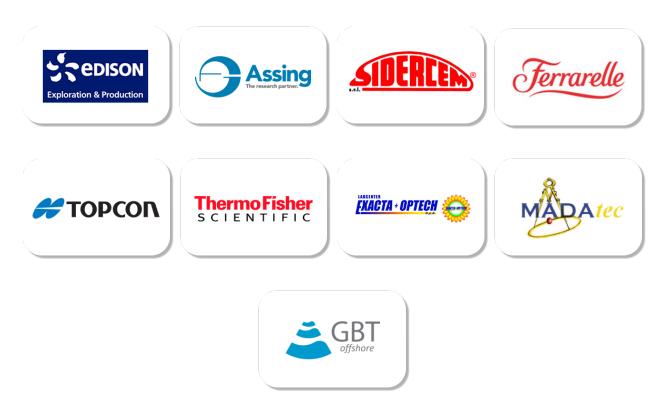
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### **PLENARY LECTURES**

#### Earthquakes and tsunamis: old and new defensive strategies between "real" and perceived hazard

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Keywords: seismic risk, Early Warning systems, seismic monitoring system.

The reduction of seismic risk has been historically faced using two approaches: the first one includes the evaluation of (long-term) hazard and the reduction of building vulnerability; the second one has focused on reducing the exposition through last minute actions, i.e., earthquake prediction / forecast. Whereas the first approach has brought to significant reduction of loss of both human lives and assets, particularly in countries where the frequency of large earthquakes is high, the second one has not, with very few lucky exceptions. In Italy, despite a long history of research and achievements in hazard studies, a high quality of seismic engineering expertise, and several "antiseismic" laws, a long-term plan of vulnerability reduction has never been really implemented. The recent earthquakes in central Italy have led to a renewed attention to the problem, but the innovation introduced by Law 232/2016 (and subsequent decrees) still appears to be a too weak stimulus to solve the problem. Reducing the exposition to earthquakes in the short term is possible in particular conditions. While the current knowledge on earthquake precursors and short term variations of seismic hazard does not allow us to devise any effective action to reduce the exposition just before an earthquake strikes, the implementation of Early Warning systems (EWS) is a viable way to reduce the impact of earthquakes (and tsunamis). For earthquakes, the time available to issue an alert, after the earthquake generation and before the strongest shaking, is very short (seconds to tens of seconds), particularly for crustal shallow earthquakes like those affecting our country. However, the enactment of some defensive actions, such as warning people and automatically securing some industrial, medical, transportation systems may contribute to save human lives and reduce damage. For tsunamis induced by earthquakes, the times to issue an alert are in the order of minutes to hours. Therefore, the effectiveness of EWS is high, provided that a rapid, effective seismic monitoring system is operational. I will describe the achievements and the criticalities of the Italian tsunami alerting system for the Mediterranean, which was established in 2017 by a Prime Minister Directive (DPCM G.U. 5/6/2017) and operates within the ICG/NEAMTWS framework of IOC-UNESCO. For both earthquakes and tsunamis, a fundamental tile towards risk reduction is people's knowledge and awareness. A continuous and more focused commitment by scientists, media, authorities, is needed in order to stimulate virtuous behaviors and effective action.

#### Contribution of Geosciences to the study and preservation of art and cultural heritage

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Keywords: Cultural heritage, conservation, archaeometry.

A brief introduction will define what Cultural heritage is from the Conservation Science point of view and will explain how the scenario changed with the advent of different materials in contemporary art. Goals of the study (archaeometry and conservation). Impact of rapid technological advances resulting in a flourishing of new instrumentation. Use of large facilities (synchrotron and neutron sources) compared to the proliferation of small portable noninvasive instruments. Composition of the Na-pyroxenes in green stone axes by a noninvasive XRD technique to determine the stone provenance, used for elucidating the trades in Neolithic Europe. Texture of the copper axe of Similaum man shed light to the metallurgy of Eneolithic period. For large facilities: Structure refinement of Maya Blue and identification of indigo in the palygorskite grooves. Use of neutrons for CT-scan of large statues (Robert van Lange), compared to powerful X-ray sources and medical equipment (Casali, Getty). For portable instruments: Ubiquitous use of hand held XRF. Advantages and disadvantages. Portable Raman, FTIR, XRF/XRD noninvasive techniques. Some examples of non-conventional applications of portable XRD. Michelangelo Last Judgment censure panels in the Sistine chapel: problem of dating the interventions with the goal of removing the most recent ones only. XRD proved to be the solution since the three painters used different yellow pigments. Discoloration of the blue sky painted with Lapis Lazuli. It was proved to be a rough partial cleaning performed using ash. Imaging has become very important: Multispectral Imaging, involving different filters and light sources from UV to IR, helps mapping the various substances on the surface. VIL, Visible Induced Luminescence, allows to take pictures of Egyptian blue only. Examples from Roman-Egyptian funerary paintings (Fayum), Herculaneum and X century Lombard church. Reflectance Texture Imaging, combines many pictures taken at different illumination angles, and allows for changing the light direction on the computer at a touch of the mouse. When X-ray Radiography in transmission is not practical, it can be substituted by Electron Emission, which involves the first 50 micrometers of surface only. SmART scan: a program that simulates XRF scanners, without the expensive equipment.

#### Large landslides as natural large scale laboratories for understanding geological processes and risks

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Keywords: landslide, hazard, risks.

Large landslides can represent a meeting point for knowledge belonging to different fields of geological sciences. The involved phenomena of rupture and evolution are made complex and controlled by the lithological, structural, physical and mechanical characteristics, by the meteorological and climatic perturbations as well as by the human action. Their size and the relationships with the morphology of slopes and watersheds can lead to different sensitivities to external factors, both natural and anthropogenic. Their presence is the answer to a complex combination of factors and they can provide the key to understanding geomorphological evolution even in distant or unreachable sites. Their observation and monitoring allow us to acquire data without which the modeling of instability risks not being representative. The evolution after the rupture and during the catastrophic collapse can be extremely varied and involves processes studied based on the characteristics of the deposits, their geometry, the degree of fragmentation and the released energy, through theoretical, numerical and scaled models, and partly on analogues of different geological phenomena. This lecture wants to highlight how around these aspects has grown and can increase the knowledge of phenomena and the behavior of materials, an interest limited not only to the geological applications and geomechanical aspects. For this purpose, examples of landslides in different contexts will be shown, highlighting how these can allow the understanding of the acting mechanisms and how multidisciplinary experimentation and observation can be indispensable tools for assessing their hazard and the associated risks.

#### IODP-Italia and the Italian participation in ECORD-IODP and ICDP

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#### Keywords: IODP-Italia, ECORD, CDP.

The *International Ocean Discovery Program* (IODP) is an international marine research collaboration that explores Earth's history and dynamics using ocean-going research platforms to recover data recorded in seafloor sediments and rocks and monitor subseafloor environments through drilling and coring. The program is currently supported by 24 countries, and it has been reshaped through time (previously DSDP-ODP-IODP).

Italy participates in IODP as a member country of the *European Consortium for Ocean Research Drilling* ECORD since its foundation in 2003. Thanks to a national funding annually allocated by MIUR since 2013, IODP-Italia now operates through a national advisory committee (IODP-Italia Committee). IODP-Italia Committee is currently composed of members from CNR, CoNISMa, OGS, INGV, and ENEA, and co-operates with the national IODP-Italia office through a scientific coordinator and the management and administrative support of the CNR Dept. of Earth System Science and Environmental Technologies.

IODP-Italia coordinates, supports, and promotes the involvement of Italian researchers in ECORD-IODP as shipboard and shore-based scientists, proponents of drilling projects, and national representatives in panels and steering committees. IODP-Italia also fosters the participation in training courses, summer schools and activities for educators and outreach specialists. All opportunities to get involved are regularly circulated through the mailing list <u>iodp-italia@cnr.it</u> and published on the website <u>www.iodp-italia.cnr.it</u>. Funding schemes to support moratorium and post-moratorium proposals on IODP samples and data will be soon published on the IODP-Italia webpage. On the website, interested researchers will find also details about the Italian participation in recent and past ECORD-IODP activities.

In 2018, the Italian participation in ECORD-IODP has so far envisaged:

- 4 Italian scientists onboard IODP expeditions (1 co-chief), ~ 10 invited to take part in post-cruise meetings and sampling parties, ~ 12 lead and co-proponents of active drilling proposals, 3 PhD students attending training courses;
- Exp. 360 post-cruise meeting hosted in Sicily by Italian shipboard scientists, ECORD Facility Board Meeting #6 held in Venice, the 2018 edition of the ECORD School of Rock organized by the Univ. of Pavia and hosted in Italy for the first time (all sponsored by IODP-Italia);
- A workshop titled "Scientific Drilling in the Mediterranean Sea" held in Rome to gather the national scientific drilling community and foster the submission of drilling proposals in the Mediterranean area (IODP-ICDP).

To emphasize and strengthen the Italian participation in the *International Scientific Continental Drilling Program* ICDP, one of the major targets in 2018/2019 for IODP-Italia includes a closer collaboration with the continental drilling community, to create a new national committee for the participation in the international scientific drilling programs ECORD-IODP and ICDP.

### **Session S1**

# Responses and dynamics of ecosystems to environmental perturbations: from local to global, from short- to long-term

Conveners AND CHAIRPERSONS Giulia Faucher (Università di Milano) Massimo Bernardi (MUSE - Museo delle Scienze, Trento)

## The Carnian Pluvial Episode and its impact on the diversification of dinosaurs and on the origin of modern terrestrial vertebrate faunas

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Keywords: Extinction, radiation, turnover.

In this contribution, we present evidence for a major inflection point in the history of tetrapods on land, a jump in the diversification of archosauromorphs at 232-230 Ma. This corresponds to a long-noted changeover in Triassic terrestrial tetrapod faunas, from those dominated by synapsids, many of them holdovers from the Permian, to those dominated by dinosaurs. We provide evidence that dinosaurs rapidly rose in diversity and ecological importance during this time, corresponding to a phase of increased rainfall and perturbation of oceans and atmospheres, the Carnian Pluvial Episode (CPE), which was followed by substantial aridification. The rock record through the CPE confirms that this event shared many characteristics with other mass extinctions driven by the eruption of large igneous provinces, in this case the Wrangellia flood basalts of the west coast of North America. If this was a catastrophic extinction event, then the environmental perturbations of the CPE explain the sharp disappearance of various terrestrial tetrapods, and the subsequent sharp rise of dinosaurs and perhaps other clades too, especially those that constitute much of the modern terrestrial fauna, such as lissamphibians, turtles, crocodiles, lizards, and mammals. We conclude that, in this view, a new model emerges whereby (non-avian) dinosaur evolution was shaped by three deep global ecosystem perturbations: they originated just after the Permian-Triassic mass extinction, rapidly diversified during the CPE, and went extinct at the end-Cretaceous extinction.

#### The effects of paleoenvironmental changes on nannoplankton biocalcification: mid-Cretaceous size variations of *Biscutum constans*

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Keywords: nannofossil, Cretaceous, biocalcification.

The investigation of the geological record allows to decipher the response of organisms to paleoenvironmental changes occurring at a time scale larger than human observation. One open issue regards the effects of stressing factors on coccolithophore algae calcification process. These planktonic organisms are important primary producers and largely contribute to the organic and inorganic carbon cycle. In the last decades, evidence for a direct response of coccolithophores to stressing factors were provided by experiments on living forms and by studies of extreme Cretaceous events, such as the early Aptian Oceanic Anoxic Event (OAE) la and latest Cenomanian OAE 2. These OAEs were marked by altered carbon cycle, trace elements anomalies, rapid and intense warming and peaks in surface water fertility. The studies evidenced fluctuations in the mean size of some selected nannofossil species, among which, Biscutum constans resulted to be the most sensitive. B. constans reached the smallest mean size under the climax of the OAEs coinciding with super greenhouse climate, excess CO<sub>2</sub>, accelerated nutrient recycling and trace metals peaks. In order to better understand the role of these stressing factor/s on B. constans calcification, we decided to investigate B. constans size variations through a longer time interval (ca. 27 Myrs) spanning the Aptian to the Cenomanian. This time interval includes either periods of stability and episodes of global environmental perturbations such as OAE 1a, OAE 1b, OAE 1d, the Mid-Cenomanian Event and OAE 2. Prior to this study, it was unknown if B. constans was affected by size changes during interludes of "stable" paleoenvironmental conditions. We focused on the Umbria-Marche Basin (central Italy)by investigating the Piobbico core and the Monte Petrano section which are stratigraphically well constrained and a complete characterization of paleotemperature and paleofertility is available. By performing morphometrics analyses we intended to better understand which factor (or combination of factors) was directly altering the biocalcification process in this species. The results revealed indeed changes in the mean size of *B. constans*. A relatively prolonged interval of smaller specimens was detected after OAE 1a. A recovery in B. constans average size was identified in the Albian although the largest specimens were found in the middle Albian. A relative decrease in size is detected just prior to OAE 1d. The subsequent main shift coincides with OAE 2 marked by dwarf specimens. Statistical analyses were performed to detect any possible dependence from temperature or nutrient variations suggesting no direct connection between these parameters and size, whilst trace elements peaks and phases of most intense volcanism resulted to correlate with minimum B. constans size.

#### The seagrass skeletal assemblage from modern to fossil and from tropical to temperate: insight from Maldivian and Mediterranean examples

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Keywords: Seagrass, foralgal, carbonate platform.

Seagrasses are marine angiosperms that form extensive submarine meadows in the photic zone where carbonate producing biota dwell as epiphytic on the leaves or as infaunal forms, constituting prolific carbonate sediment factories. As seagrasses have a low preservation potential and records of exceptionally well preserved and plant material from marine settings are rare, these paleoenvironments are difficult to identify in the rock record. Consequently, sedimentological and paleontological proxies are the main indicators of the presence of seagrass-dominated ecosystems. In this work we investigate the skeletal assemblage of Modern (Maldivian and Central Mediterranean) and fossil (Eocene, Apula and Oman Carbonate Platforms and Oligocene, Malta Platform) seagrass examples to characterize the skeletal assemblage of modern and fossil seagrasses. Two main types of grains, calcareous algae and foraminifers, constitute around the 50% of the bioclastic sediment in both tropical Maldivian and temperate Mediterranean scenarios, However, in the tropical setting they are represented by the green algae (Halimeda), while in the Mediterranean by corallinacean red algae. In contrast, in the Eocene examples, the foraminifers are the most conspicuous group, and the green algae are also abundant. The opposite occurs in the Maltese Chattian, which is dominated by coralline algae (mean 42%) and the foraminifers are still abundant. We suggest the use of the term foralgal to identify the seagrass skeletal assemblage. To discriminate between red algae and green algae dominance, we propose to introduce the prefix GA (green algae) and RA (red algae). The investigated examples evidence that the GA-foralgal is typical of tropical, not excessively dense seagrass meadows, characterized by a well-illuminated substrate to support the development and calcification of the Halimeda thalus. Contrarily, the RA-foragal is typical of seagrass tropical to subtropical meadows very dense to create oligophotic conditions in the seafloor or of temperate settings where Halimeda cannot calcify.

### The central Mediterranean carbon isotope record across the Eocene-Oligocene transition: the inorganic vs the organic carbon isotope signals

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Keywords: C-cycle, Cenozoic, Majella.

The Eocene-Oligocene transition represents a fundamental step in the evolution of the modern climate since it marks the last greenhouse-icehouse transition faced by the Earth. In this work we present the upper Eocene to lower Oligocene  $\delta^{13}C_{Carb}$  and  $\delta^{13}C_{TOC}$  records of a shallow-water and a hemipelagic carbonate settings within the central Mediterranean area. The shallow-water, bulk-rock carbon isotope signal has been analysed in the northern portion of the Apula Platform, cropping out in the Majella Mountain, central Apennines (Santo Spirito Formation). A coeval Umbria-Marche basinal succession has been investigated in the Massignano section (Conero area, central Italy), where the Total Organic Matter (TOC) carbon isotope record has been analysed and discussed. This work aims to (i) discriminate between the global and the local signature of the C-isotope record before and during the Oi-1 event; (ii) correlate the regional C-isotope signal with the global record; (iii) evaluate the carbon cycle dynamics across this major greenhouse-icehouse transition. The upper Eocene carbon isotope record of the analysed successions matches with the global signal. The shallow-water  $\delta^{13}C_{Carb}$  record of the upper Eocene shows an overall negative trend, whereas the contemporary  $\delta^{13}C_{TOC}$  records a positive one. The decoupling of the two curves is related to the reduced fractionation effect by primary producers during the late Eocene due to the decreasing pCO<sub>2</sub> after the C-cycle perturbation of the MECO, and before the onset of the carbon anomaly linked to the Oi-1 event. However, regional factors superimposed to the global forcing influenced the Neo-Tethys carbon isotope record, as suggested by several transient negative spikes that mark the  $\delta^{13}C_{TOC}$  record of the Massignano section. These negative spikes are interpreted as short times of higher productivity linked to enhanced nutrient availability and triggered by the westward subtropical Eocene Neo-Tethys current entering from the Arabian-Eurasian gateway. In contrast, the shallow-water record does not display these short-term productivity pulses. A change in the carbonate factory is only recorded at the Eocene-Oligocene transition, marked by a reduction of the larger benthic foraminifera and the spread of seagrass and corals. Moreover, in the shallow-water record of the Santo Spirito Formation, no major carbon isotope shift related to the Oi-1 event is recorded due to the presence of extensive slumps that disrupt the bedding. These slumps are the main evidence of the sea-level drop that occurred concomitantly with the onset of the Antarctica ice-sheet, which caused the deepening of the storm-weather wave base and increased the instability over the entire ramp.

#### Planktic foraminiferal response to the ETM2 in the Tethys realm: upper water column disruption and marked dwarfism

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Keywords: Early Eocene hypertermal, planktic foraminifera, environmental changes.

The hyperthermal event Eocene Thermal Maximum 2 (ETM2, ~54 Ma) is recorded at the Madeago section (NE Italy) as documented by the calcareous plankton biostratigraphy. This section deposited in a middle-lower bathyal setting of the central-western Tethys. Records on planktic foraminifera, that are important calcifiers and an extremely sensitive class to environmental changes, are scarce across this event that is one of the major hyperthermal of the early Paleogene. We present here the integrated geochemical ( $\delta^{13}$ C and  $\delta^{18}$ O) and planktic foraminiferal record across this event. Our data on planktic foraminiferal assemblages shows significant, though transient, changes across the ETM2, indicating abrupt environmental perturbations. The changes consist of marked increased in warm indices, surface-dweller acarininids and decline of chiloguembelinids and deeper-dweller subbotinids. We interpret these variations as due to the ETM2 impact on the entire upper water-column and possibly related to subsurface warming that produced a contraction of ecological niches. An extraordinarily pronounced dwarfism (up to more than 50%) of planktic foraminiferal tests involved both surface- and deep-water dwellers at the Madeago section during the ETM2. Planktic foraminifera achieve their maximum size within their preferred water mass and size decreases away from such optimum conditions thus dwarfing implies extreme environmental stressors as recorded during biotic crisis, mass extinctions or preceding the extinction level. Multiple causes can induce reduced size in planktic foraminifera. They may include collapse in primary production, adaptation to decrease sinking rate within less dense warmer waters, changes in salinity and temperature, decrease in oxygen levels and loss of symbiotic relationship (bleaching). Whether transient bleaching could explain the symbiont-bearing morozovellid and acarininid dwarfing it cannot justify the reduced size of the asymbiotic subbotinids. Other causes may include temperature increase that accelerates protists metabolism thus requiring more oxygen but dissolved oxygen concentration decreases in warm waters. Expanding the ratio of surface area by reducing the cell mass can be therefore a strategy to optimize resource uptake. Furthermore, recent culturing and open ocean observations suggest that acidification affect preferentially larger planktic foraminifera and diminish their calcification. Consequently, drop in pH may have influenced test sizes across the ETM2. The short-term ETM2 negative d<sup>13</sup>C shift implies addition of CO, to the ocean and atmosphere and may have caused upper-water column acidification. Interestingly, biotic recovery rates were slower with respect to the carbon cycle as planktic foraminiferal disruption, included dwarfism, persisted during the  $\delta^{13}$ C recovery phase. This evidence has important repercussions in view of the current carbon-cycle anthropogenic disruption.

#### New insight on the nature of iron Ooid formation - a study from Panarea island (Sicily, Italy)

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Keywords: Panarea Island, iron-ooids, hydrothermal fluids.

In spite iron ooids are sedimentary particles widely documented in the fossil record, they are extremely rarein modern settings. The origin and genesis of fossil iron ooids and oolitic ironstones, and their extensive distribution, have long been a matter of debate and controversy (e.g., Ferretti, 2005), invoking both abiotic processes (e.g., Sturesson, 1992) and biologically induced mechanisms (e.g., Burkhalter, 1995).

A modern iron ooidal deposit was recently discovered and sampled in the marine shallow-water settings off the coast of Panarea, in the Aeolian Islands, by INGV and ISPRA teams. This exceptional discovery offers an extraordinary opportunity to answer many open questions on fossil analogues. With this contribution we intend to better elucidate the iron ooids origin by studying the ooids-sand from Panarea. To reach this goal, a multi-proxies integrated approach was applied, based on morphological, compositional, and geobiological characterizations.

The Panarea deposit consists of coarse-grained, unconsolidated sand with a whitish biogenic component (mostly foraminifera and sponge spiculae) and dark brown rust ooidal grains. The results show that Panarea iron ooids perfectly match their fossil counterparts. They were formed by the deposition of iron oxyhydroxides (mainly goethite) in concentric laminae around nuclei represented by pyroclastic particles and, more rarely, by sponge spicules or other skeletal components. The spherical laminated structure resulted from the constant agitation by degassing of  $CO_2$ -dominated fluids through the seafloor sediments. Any sound evidences of microbial-mediated micro-texture (such as cell remain or induced structures, as biofilm, already reported from other hydrothermal environments including the Panarea area (Bortoluzzi et al., 2017; Esposito et al., 2018), were found. Our results allow constraining an abiotic mechanism and excluding a microbial contribution in the iron ooid formation process.

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## *Emiliania huxleyi* sensitivity to ecological changes: a new methodological approach to ascertain if and which environmental parameter influences coccolith sizes and shapes

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Keywords: calcification, morphometry, coccolith.

Coccolithophores are a group of unicellular marine phytoplankton primary producers of biogenic calcite in the open ocean. During their diploid life-cycle stage, coccolithophores produce calcite plates called heterococcoliths. These circular to elliptical coccoliths have very ornate structures and form an exoskeleton, called coccosphere, generally composed of a single layer of plates. Coccolithophore algae produce coccoliths one at a time, with an intracellular growth process. This begins with nucleation of a proto-coccolith ring of simple crystals and continues by upward and outward growth of these crystals into a complex unit to form complete coccoliths. Coccoliths are then extruded to the cell surface and continue to be generated until a complete coccoliths occur if the growth process is arrested due to premature extrusion of the coccolith from the cell, while malformation is due to "irregular coccolith formation as a result of departure from the normal growth process" (Young and Westbroek 1991), implying the malfunction of the coccolith-shaping machinery per se. Malformations are difficult to evaluate and most studies use a qualitative and subjective approach with the identification of arbitrary categories (e.g. normal, very malformed, malformed and incomplete coccoliths).

The use of morphometrics has the potential to significantly improve the knowledge of shape and size variations in coccolithophore taxa and the ability to describe their evolutionary history and response to ecological changes. Here, we present a new morphometrical method to quantitatively characterize coccolith sizes and shapes and discriminate normal versus malformed specimens and the degree of malformations. This methodology was applied to coccoliths of *Emiliania huxleyi* grown under different ecological conditions. The obtained results evidenced that *E. huxleyi* is very sensitive to chemical alterations of seawater and specifically, that introduction of toxic trace metals and increased  $CO_2$  concentrations might have the potential to disturb the calcification process causing an increase in the number of aberrant coccoliths, an alteration of the calcite content per coccolith and a general decrease in the cellular calcification rate.

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#### From autochthonous Micrite to Aphanodolomites: the key role of microbialites in dolomitization processes

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Keywords: microbialites, dolomites, diagenesis.

On the basis of the formation mode dolomites can be divided into two groups: primary and secondary. The primary dolomite precipitates directly from aqueous solution through microbial activities, the secondary dolomite is a diagenetic product formed from a precursor carbonate mineral (calcite or aragonite) through a dolomitization process. Most assessments on the secondary dolomitization have dealt with supplying magnesium to the system while the type of carbonate precursor was not sufficiently considered. Here we discuss the possible influence of the micrite type, autochthonous versus allochthonous, on secondary dolomitization processes. The recrystallized and dolomitized Rifugio Vallandro section and the isochronous Carnian erratic boulders of Alpe di Specie (South Tyrol, Italy) offer a unique example to study the relationships between microbialites and secondary early dolomitization processes. The Rifugio Vallandro section contains at least three frame-builder horizons, in part constituted by deeply dolomitized boundstone, with corals in life position, sponges, chaetetids and stromatoporoids. Peloidal crusts and aphanitic fine texture, showing organic matter relics, suggest microbial mediated mineralizations. Geomicrobiological characterization of microbialites from Alpe di Specie indicates the presence of Sulfate Reducing Bacteria biomarkers, the lack of specific molecules typical of cyanobacteria, and REE consistent with suboxic conditions (Tosti et al., 2014). The SRB biomarkers can be associated to clotted-peloidal fabrics, which resemble those commonly present in younger skeletal/ microbialite pendant bioconstructions (Guido et al., 2013). Similar processes can be hypothesized for the primary carbonate matrix of Rifugio Vallandro patch reefs. On the basis of the grain size two components can be distinguished in the matrix: aphano- and coarse crystalline textures. Remains of peloidal fabric are still observable. The sample of Rifugio Vallandro suffered pervasive dolomitization. Trace of organic matter allows attributing the aphano-crystalline dolomite to primary autochthonous micrite (microbialite), while the coarsecrystalline dolomite seems to derive from the primary allochthonous micrite for the presence of large amount of siliciclastics and the absence of organic remains. The study on the control of dolomitization processes by different type of primary micrites could open a new window on the interpretation of dolomitization processes of ancient bioconstructions.

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#### Zinc incorporation in marine bivalve shells grown in mine polluted seabed sediments

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Keywords: Biominerals, bivalves, zinc incorporation.

More than 70 different types of biominerals have been identified in different Earth environments, and these are characterized by different chemistries that evolved in the formation of various biological hard tissues. Among marine biominerals, bivalve shells are characterized by great potentialities as environmental proxies, because these organisms record environmental changes in their mineralized shells.

Previous literature has shown that bivalves accumulate trace elements from the external environment and that Zn detoxification in bivalves can occur by Zn deposition in the mineral structures (shell and/or microspherules; Lopes-Lima et al. 2012). Despite the rapid development of the research in the last few decades, to date, the coordination environment of Zn incorporated into the biomineralized shell has not yet been investigated though it represents a fundamental knowledge in order to assess the nature of Zn biomineral phases and the biological mechanism involved in the detoxification. In our study, chemical analysis, X-ray diffraction, transmission electron microscopy, X-ray absorption spectroscopy and soft X-ray microscopy combined with low energy XRF mapping were applied to investigate Zn incorporation in different bivalve genera (*Donax, Glycymeris, Lentidium* and *Chamelea*) collected from environments affected by past mining activities (Malfidano mining district, SW Sardinia, Italy).

Investigated bivalve shells are mainly made up of aragonite and the most abundant trace metals are Zn (2.0-81 mg/kg), Fe (5.4-60 mg/kg), Pb (85-350 mg/kg) and Mn (0.5-4.5 mg/kg). Here, we focus on Zn revealing by X-ray Absorption Near Edge Structure analysis that, for all the investigated genera, Zn occurs as independent Zn phases, and it is not incorporated or adsorbed into the aragonitic lattice. Linear combination analysis shows that Zn phosphate is the most abundant species in *Donax* and *Lentidium* genera. Zn cysteine fraction increased (up to 56%) in the *Chamelea* shell samples that show the highest Zn concentrations (80 mg/kg). Also, Zn hydrate carbonate (hydrozincite) was found to occur in the shells.

Variation in the Zn chemical environment suggests that bivalves have developed different biogeochemical mechanisms to regulate Zn distribution and speciation inside the shell, and that cysteine plays a significant role as active part of the detoxification mechanism.

In addition to the environmental significance of bivalve shells, achieved results are relevant to clarify biomineralization processes resulting as defense strategies in polluted environments. Clarifying these processes represent a useful tool to understand how bivalve shells can be employed in i) paleoproxy applications and ii) monitoring environmental conditions.

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#### Factors affecting Uranium distribution in early Permian-late Variscan Sardinian basins: chemical and γ-ray data constraints

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Keywords: Uranium, Palaeo-environmental proxies, Sardinia.

The late, post-collisional evolution, of the European Variscides resulted in both extensional and transtensional dynamic responsible for volcanic and plutonic activity, development of intracratonic basins and overall high thermal flow. Between late Carboniferous and early Permian, equatorial conditions promoted the diffusion of rainforests that, inside the subsiding basins, gave rise to accumulations of organic matter and coal seems. The transition from the dark, reducing, organic matter-rich facies to red beds is not sharp, and traditionally has been related to drier conditions and to a new different palaeogeographic frame.

The red bed-arid climate paradigm has been questioned in the Sardinia Permian basins (Sinisi et al., 2014 and references therein), whereas in other Variscan sites the dark facies-red beds dualism was referred to the subsidence history of the basin. Several geochemical and mineralogical proxies (e.g. REEs contents, V/Cr and Zn/Cu elemental ratios, and occurrence of both Fe-oxyhydroxides and phyllosilicates) have been used in order to establish environmental conditions in terms of sediments and terrane provenance, palaeoredox and draught/ wet balance.

With this in mind we investigated a robust multielemental chemical dataset of sediments (n=56) having different grain size and different colour assuming the dark facies as broad proxy of wet vegetated environment, red beds as indicator of arid conditions and U/Th as palaeoredox indicator. The sampled successions consist of proximal to distal alluvial fan and lacustrine deposits. The U content in the sampled sediments ranges between 0.9 and 22.3 ppm with a median value of 3.95, higher than the average value associated to the Upper Continental Crust models (UCC: 2,80 ppm, Taylor & McLennan 1985; GLOSS: 1,68 ppm, Plank & Langmuir 1998). Univariate statistic allowed to individuate outliers (11-22.3 ppm) indicative of a reducing episode. This finding is supported by several  $\gamma$ -ray data (HPGe detector) that confirm the occurrence of an uranium-rich level. Principal Component Analysis (PCA), performed on the devoid database instead, suggests that U distribution is controlled by a mechanism mostly depending on differences in source areas.

Finally, no meaningful differences have been observed in palaeoredox conditions between the red and grey siltite, as hematite - the sole Fe- oxidised phase detected - is stable in a wide range of Eh-pH conditions.

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#### Oligotypic Microbial-Metazoan dominated carbonate platform evolution during upper Triassic rifting (northern Calabria-Italy)

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Keywords: Carbonate facies, Stressed environment, Microbialite.

The Norian-Rhaetian of Northern Calabria consists of three depositional sequences: Corvino (Cds) (Early-Middle Norian), Vaccuta (Vds) (Middle-Upper Norian), and Grisolia (Gds) (Rhaetian), representing a carbonate platform system successively drowned (Perri et al., 2003; 2017). In the first two sequences, two different oligotypic fauna/flora associations have been distinguished: microbialites-sponges-serpulids dominate the Cds, whereas bivalves-microbialites dominate the Vds. In particular Cds, interpreted as a deep rimmed platform, is characterized by a deep bioconstructed margin in which a genus of sphinctozoan sponges results the main framebuilders and is associated to serpulids, one species of udotacean algae and microbialites. Inter-supratidal environments in the inner-platform of the Cds are dominated by flat to domal stromatolites and thrombolites, affected by frequent subaerial expositions; in subtidal environments microbialites form high relief bodies sometimes associated with megalodontid bivalves. The outer-platform is mainly characterized by a slope constituted by debrites, mainly turbidites and slumps, associated with pelagic sedimentation. The Vds is interpreted as a ramp-type platform, in which sand barriers protect inner ramp lagoonal to supratidal environments. In particular, a species of isognomonid bivalves (Isognomon exilis) colonized the sand bodies associated with encrusting forams, rare gastropods and low relief microbialites. The latter form relatively high relief buildups in the subtidal settings where serpulids are also present. The outer ramp is characterized by mudstones and storm beds. Lastly, the Gds is characterized by carbonate storm beds, fine-grained turbidites and rare slumps, intercalated to thin bedded mudstones, marls and shales.

The fauna/flora assemblage characterizing the Cds and Vds implies general environmental stressed conditions through the whole Norian, characterized by limited water circulation, anoxia, high salinity and eutrophy. These environmental conditions are most probably due to the interplay between climate factors and multiple syn-depositional trans-tensional tectonic pulses, and less to eustatic sea level variations, which induced the opening and the progressive deepening of intra-platform basins (to which these platforms faced) with limited connections with the open ocean. In fact, the three studied sequences can be defined as Tectonically Controlled Depositional Sequences (TCDS) in which sequence boundaries are absent: Cds and Gds represent high stand system tracts, whereas Vds a transgressive system tract.

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#### Calcareous nannoplankton response to climate variability during Marine Isotope Stage (MIS) 19 in the SW Pacific

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Keywords: calcareous nannoplankton, Marine isotope Stage 19, Carbon Cycle.

Calcareous nannoplankton are one of the major components of the marine phytoplankton and they are at the base of the food web and play a major role in the carbon cycle. The scientific community is constantly in search of past warm time intervals, better known as interglacials, in order to identify potential analogues of the modern global warming. In this work, we aim to analyze the response of nannoplankton to the climate conditions of interglacial Marine Isotope Stage (MIS) 19, with the final aim to understand the adaptive strategies of this marine group.

We present here a high-resolution study of nannoplankton assemblages derived from ODP Site 181-1123 in the SW Pacific (42.7862 N; 171.499 E). We analyzed 69 samples spanning from MIS 20 to MIS 18 (814 ka and 742.6 ka). These samples were prepared according to standard procedure for Light Microscopy (LM) identification at the University of Pavia. For each sample, a minimum of 500 specimens was counted to derive the relative and absolute abundances, and a total of 21 taxa was recognized in the assemblage. The morphometry (size, width, mass and surface of the shield) of the species belonging to the two most abundant genera (*Gephyrocapsa* and *Reticulofenestra*) was investigated at the Institute of Environmental Science and Technology (UAB, Barcelona) through an automated system of coccoliths recognition (SYRACO). Although this version of SYRACO was not able to differentiate the 2 genera, it distinguished two classes: the small placoliths with a shield length ranging from 1.7 to 2.1  $\mu$ m and the big placoliths with a shield length ranging from 1.9 to 2.7  $\mu$ m. These data taken together with the others morphometric parameters allow to assess the calcification degree of these two abundant genera during MIS19. Moreover, the comparison of our data with the reconstruction of atmospheric CO<sub>2</sub> concentrations (CO<sub>2tam</sub>) and sea surface temperatures (SST) shed light on the dynamics of both the primary and carbonate pumps during this warm interval.

The assemblages were, in general, well preserved throughout the record and dominated by small specimens (size<3,5  $\mu$ m) belonging to the genera *Gephyrocapsa* and *Reticulofenestra*. During the MIS 19, in parallel to the increase in SST (about 8°C) and CO<sub>2atm</sub> we noticed a strong decrease in absolute abundance and a relatively higher species richness. In the same interval, the data from SYRACO evidenced a decreasing trend for both the small and big placoliths, the smallest specimens being on average more abundant. Moreover, the ratio mass/surface, used here as a calcification index, showed higher variability during the MIS 19. Therefore, preliminary results highlight that both warmer surface waters and higher CO<sub>2atm</sub> are responsible for less abundant nannoplankton and for a reduction in calcification, at least for the smallest specimens, underlining a weakening of the nannoplankton role in the primary and carbonate pumps during the MIS 19.

# The oldest and more complete tapinocephalid dinocephalian from Africa: postcranial skeleton *Tapinocaninus pamelae* (Synapsida: Therapsida)

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Keywords: postcranial skeleton, Dinocephalia, Permian.

Dinocephalians, which comprise an important component of Middle Permian tetrapod biodiversity, are a crucial clade of Pangaean basal therapsids. While most studies over decades focused on the skull, postcranial research has lagged, largely because of the paucity and unwieldy size of specimens. The discovery and full state of preparation of an almost complete skeleton of the basal tapinocephalid dinocephalian *Tapinocaninus* from the rocks of the lowermost Beaufort Group of South Africa for the first time allows a detailed description of post-cranium in this taxon and an accurate vertebral count for a dinocephalian. The study presents the first quantitative dinocephalian long bone morphometric analysis and shows that in *Tapinocaninus pamelae*, long bones are autapomorphic in several features within the morphospace explored by dinocephalians. The new data and results enable discussion on morphology the appendicular skeleton and a new reconstruction of the posture in tapinocephalids. Although demonstrating several apomorphic characters, the skeleton retains pleisomorphic anatomical features previously described only in "pelycosaur"-grade synapsids, (especially with regards to the axial skeleton). The discovery greatly advances understanding of the postcranial morphology of tapinocephalid dinocephalians and provides input on the enigmatic phylogenetic relationships of early therapsids.

# Correlation between extinction pattern and $\delta^{13}$ C fluctuations across the Triassic Jurassic boundary in shallow water settings: a proxy for the present day acidification processes

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Keywords: Triassic-Jurassic boundary, Mass extinction, Carbon isotopes.

With the aim to assess the possible influence of the  $\delta^{13}$ C variations on the benthic communities across the Triassic Jurassic boundary we have carried out sedimentological, biostratigraphic and stable isotope studies on an about 220 m thick peritidal section cropping out in Northwestern Sicily (San Vito Lo Capo peninsula).

The subtidal facies of the lower and middle part of this succession show the common occurrence of large and thick megalodontids and a benthic foraminiferal assemblage with *Triasina hantkeni* and Aulotuortids that support a Rhaetian age. In the lower part of the succession, a sudden reduction of the size, shell thickness and abundance of the large megalodontids witnesses a first significant biotic perturbation. This "Lilliput effect" corresponds to a first severe negative shift of the carbon curve that match a perturbation recorded worldwide and known as "initial CIE". The "Lilliput effect" does not seems to have any influence on the microbenthic community (e.g. foraminifers and calcareous algae).

Upward, a second negative excursion spans a large stratigraphic interval and consists of at least 4 subtrends. This negative excursion is well comparable to the "main CIE" as defined worldwide in several sections. In our section, the lower part of the main CIE corresponds to the disappearance of the megalodontids, while the upper part of the main CIE records the LO of the microbenthic communities and, in particular, of the *Triasina hantkeni* assemblage.

Upward, concurrently to a gradual positive trend of the carbon curve (ca. +1‰) a gradual recovery of the benthic communities occurs, as witnessed by oligospecific assemblages of the problematic calcareous alga *Thaumatoporella parvovesiculifera* and, subsequently, by the appearance of benthic foraminifers such as *Siphovalvulina* sp.

A comparison between the  $\delta^{13}C_{carb}$  curve from the studied section and several coeval  $C_{carb}$  and  $C_{org}$  curves from carbonate platform, ramp and deep basins successions, shows a similar isotopic trends, however with a diverse magnitude and response of the benthic communities. This confirms the influence of external forces such as CAMP volcanism on the carbon fluctuations that leaded to the end Triassic extinction (ETE). The effects of the T/J carbon fluctuations on the benthic communities could represent a proxy for the present day acidification processes that are affecting the carbonate calcifiers organisms.

#### Calcareous nannofossil paleoceanography across the Toarcian Oceanic Anoxic Event: a story of fertility and acidification (Sogno Core, Lombardy Basin, Northern Italy)

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Keywords: Toarcian Oceanic Anoxic Event, global change, nannoplankton resilience.

The Toarcian Oceanic Anoxic Event (T-OAE) represents a global extreme perturbation of the oceanatmosphere system evidenced by geochemical anomalies, severe changes in the chemistry of the ocean and largest response of marine biota. In Western Tethys the T-OAE is represented by a black shale interval (locally named Fish Level) associated to a carbonate crisis. In the Early Jurassic, calcareous nannoplankton were already a main producer of pelagic micrites and, consequently, changes in nannofossil assemblages can help disentangle surface water conditions relative to global to local perturbations.Nannofossil investigations were performed on the Sogno Core that recovered a 27 meter-thick stratigraphic section (upper Pliesbachian-lower Toarcian): excellent quality of cores allowed a high-resolution sampling for multidisciplinary characterization of changes prior to, during and after the T-OAE.

Quantitative and morphometric analyses of Schizosphaerella punctulata and Mitrolithus jansae identified changes in abundance, size and/or morphologies: both taxa display a major decrease in abundance at the onset of T-OAE and remain rare through the interval of perturbed conditions. Only S. punctulata shows a recovery at the end of the T-OAE, while M. jansae barely survived the paleoenvironmental stress and disappeared soon after its termination. S. punctulata shows a decrease in size across the T-OAE possibly as a result of higher fertility combined with some acidification. Contrarily, M. jansae does not show significant size decrease across the T-OAE. Calcareous nannoplankton were influenced by increased nutrient availability, warming and excess CO<sub>2</sub> that concurred to the dramatic shift in assemblage composition. Complex global changes contributed to the establishment and maintenance of very stressing surface waters favouring opportunistic taxa. The period preceding T-OAE was a time of prolonged stability and oligotrophy promoting a diversified calcareous phytoplankton community with abundant k-selected deep- and intermediate-dwellers. Then, the T-OAE was marked by meso-eutrophic conditions, locally associated to accelerated run-off favoured opportunistic taxa: both heavily calcified S. punctulata and M. jansae experienced a major decrease in abundance and the former taxon also underwent reduction in size while taxa producing smaller and less calcified coccoliths were favoured. Stressing conditions started in the latest Pliensbachian and triggered subsequent changes in nannofloral composition and structure recorded worldwide suggest that the environmental perturbations preceding and accompanying the T-OAE possibly stimulated biomineralization of new coccolith morphologies. After the T-OAE, paleoceanographic conditions, at least as far as the photic zone is concerned, only partly and gradually returned to a pre-perturbation state suggesting that the deepening of the nutricline and re-establishment of stability required a long period after anoxia terminated.

### Session S2

### Deciphering ancient paleoenvironmental perturbations and their impact on the marine ecosystems

Conveners AND CHAIRPERSONS Francesco Dela Pierre (Università di Torino) Francesca Lozar (Università di Torino) Alessandra Negri (Università Politecnica delle Marche)

#### Big Data in Geoscience: a new approach for the study of sapropel S1 in the Mediterranean Sea

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Keywords: Big Data, Geosciences, Mediterranean Sea.

Science advances and with it the storage of large amounts of data. The need to use this data efficiently, quickly and safely is possible thanks to the Big Data science that allows us storage and relationship data in order to obtain new knowledge. Various discipline of science such as ecology, health or genetic have published numerous articles about the advantages of Big Data and the need to train in this field for better comprehension and use. Aim of my project, is to take advantage of Big Data for the study of the sedimentary layers that occurs in the Mediterranean Sea called Sapropels. The objective of this work is to find new patterns that help researchers to understand the mechanisms of Sapropel formation. In order to achieve new results, a deep knowledge of the sapropel dedicated literature is needed together with basic skills of softwares for managing the huge amount of data stored either in the web or still in the hands of researchers. This allowed me to realize the Entity-relationship (E-R) model of the database that permits to relate the data and to avoid errors in the introduction and extraction of them. In the last phase, I have introduced the data of the publications in the database. The introduction of data is a continuous work since the more data we have the more reliable results we will obtain. A further step, although contemporaneous to the implementation of the database, is the design of queries that allows to compare the data in search of new relationships or previously undiscovered patterns. Although a brand new approach, Big data in Geoscience is growing and reveal a great potential to exploit the high diversity of data due to the ability to search into massive amounts of information to reveal hidden patterns. For this reason, it is important to set up a scientist community able to manage this discipline in order to adopt this approach for future work.

#### Highly dynamic redox condition and fluid source identification in seep impacted sediments revealed by Mo-U enrichments, 87Sr/86Sr and REE pattern (Miocene, Mugello outcrops, northern Apennines)

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Keywords: Seep-carbonates, seepage dynamics, redox perturbations.

Cold seeps have been increasingly identified along all continental margins by geophysical surveys focused both on the characterization of seafloor structures such as pockmarks, mud volcanoes, seep-carbonates, and imaging of methane plumes within the water column. Cold seeps are very dynamic systems typically associated with high concentration of reduced compounds (H2S, CH4) in fluids, which can produce anoxic and euxinic conditions in bottom waters and in the upper sedimentary column. Seep-carbonates have been proved valuable recorders of past redox conditions, in particular, the geochemistry of trace elements and the radiogenic Sr isotope composition are used to reconstruct seepage intensity and constrain the fluid source.

Here, we combine Sr isotopes and trace element analyses (rare earth elements and Mo, U) in Miocene seep carbonates (northern Apennines, Italy) to characterize different fluid sources of radiogenic Sr and dynamic seepage conditions. The carbonate bodies formed within hemipelagites in the Marnoso-arenacea Fm. on a thrust-related anticline at the front of the Apennine accretionary wedge. The dominant authigenic carbonate phases are micrite matrix and sparry calcite filling fractures, composed of low-Mg calcite. Carbonates are affected by negligible diagenetic alteration, as deduced by Mn and Sr concentrations, so we assume that they retained the original isotopic composition of precipitating fluids. The 87Sr/86Sr ratios in carbonates vary between 0.708659 and 0.709132. Most values in micrite fit within the range of Middle Miocene seawater (Langhian), in agreement with nannofossil biostratigraphy of the host sediments, thus reflecting precipitation of seep carbonates at shallow depth within sediment, close to the seafloor. Highly radiogenic Sr values were obtained in sparitic calcite filling fractures and in micrite from conduit-rich facies at the base of the carbonate body. This signature reflects the contribution of a deeper radiogenic fluid source and the interaction of fluids with detrital clays during the fault-controlled upward migration through underlying terrigenous turbidite successions..

Carbonates show strong molybdenum and uranium enrichments (2.9 < MoEF < 275.5 and 0.6 < UEF < 41.6) thus indicating highly dynamic suboxic conditions, episodically euxinic and restricted to porewater. The shale-normalized REE patterns display the typical positive Ce anomalies and a moderate MREE bulge. The combination of 87Sr/86Sr, REE and Mo-U systematics may be a useful tool to identify seep-related redox perturbations that locally superimpose basin environmental conditions.

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Keywords: Shallow-water resedimented levels, Jurassic, Umbria-Marche Basin.

A geological mapping project was performed in three sectors of the Umbria-Marche Apennines (Central Italy), targeting the local Meso-Cenozoic succession: the Narni-Amelia, Sabini and Sibillini Mts. (Mt. Pennino Ridge). During our field-work we focused on pelagic carbonate platform (PCP)-basin systems analysis, with the aim of demonstrating how the Early Jurassic rift-related submarine topography forced the pathways of resedimented neritic material sourced by coeval active carbonate factories. Four stratigraphic sections for the northern sector of Sibillini Mts. and six for the Narni-Amelia and Sabina areas were measured. While calciturbidites are not unexpected in the Sabina region, due to the presence of the neighbouring Latium-Abruzzi carbonate platform (LACP), their presence in far removed basinal settings is less obvious. Resedimented shallow-water carbonates embedded in Middle and Upper Jurassic cherty pelagites (Calcari e Marne a Posidonia, Calcari Diasprigni and Maiolica Fms.) were discovered and mapped for the first time in the study sectors. The Middle-Upper Jurassic calciturbidites are graded and laminated grainstones-to-wackestones, locally rudstones, bearing loose shallow-water material. Coated grains (ooids, oncoids), peloids, aggregate grains, skeletal grains and benthic foraminifers are dominant, associated with typical pelagic elements (thin-shelled bivalves, radiolarians, crinoids). The neritic elements must have been sourced from productive carbonate platform(s), as intrabasinal highs had all drowned in the early Pliensbachian. The LACP is the prime suspect source-area for calciturbidites of both the Narni-Amelia-Sabina and Sibillini Mts. but shedding from carbonate platforms buried under the Adriatic Sea cannot be excluded for the Mt. Pennino area. The rugged palaeotectonic architecture inherited from the Early Jurassic rifting affected the dispersal pattern of calcarenites. The marginal palaeoescarpments of PCPs formed obstacles to the gravity flows as sediment load was discharged at their toe. The Sabina Plateau is an instructive case example: while certain W-directed flows were vigorous enough to climb its E-facing escarpment, leaving overbank deposits on its top, a "shelter" effect was by far dominant, as evidenced by the resediment-free nature of the basin lying west of it, which had to be shielded by the Plateau. To the north of the Sabina Plateau, the LACP-sourced flows were funnelled towards the Narni-Amelia area along a westward-branching arm of the Sabina Basin ("Terni corridor"). A comparable picture is observed in the northern Sibillini Mts., where calciturbidites were funnelled into a circa N-S-trending basin (Mt. Vermenone-Scurosa Valley basin) due to the presence of several PCPs, while "clean" onlap-successions characterize the northern flanks of the horst-blocks, suggesting a shield effect.

#### Lithostratigraphy and facies architecture of a Lower Permian continental succession in Central Southern Alps (Orobic Basin, Italy)

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Keywords: Lower Permian, Southern Alps, Orobic Basin.

The Lower Permian Pizzo del Diavolo Fm. of the Orobic Alps (Laghi Gemelli Gr., upper Collio Fm. *Auct.*) records, along an E-W area more than 50 km long, events that occurred in a complex continental depositional system, during semi-arid climatic condiitons and in a transtensional tectonic setting. This formation postdates intense volcanic activity and overlays parts of a large caldera and its vast surrounding areas, covered by dominating pyroclastic deposits interbedded with rare braid-plain and lacustrine sediments (Cabianca Volcanite). Post-volcanic sediment distribution reflects the existence of connected half-grabens, characterised by transverse sedimentary input (coarse-grained alluvial fans) evolving into fine-grained heterolitic deposits in the depocentre, hosting ephemeral playa-lakes.

Field mapping of two marginal sectors of the Orobic Basin (Pizzo dei Tre Signori massif and Lake Barbellino area), coupled with facies analysis of the Pizzo del Diavolo Fm., led to the identification of significantly different sedimentary evolutions. At the eastern and western ends of the basin, the Pizzo del Diavolo Fm. consists of alluvial fan and floodplain facies associations that differ from the previously studied stratigraphic architecture described in the central part of the basin. The southern borders of the studied areas are characterised by coarse-grained, fining-upward alluvial fan deposits (Val Sanguigno Conglomerate) at their base. The petrographic composition of the conglomerates from the northern border of the basin (Ponteranica Conglomerate) indicates differences in the exposed and eroded rocks from the northern and southern highs, with changes along the basin borders, where conglomeratic units with dominating basement clasts (Mt. Aga Conglomerate) occur. Floodplain facies are similar all along the basin, even if with thickness changes (up to 700 metres in the western part).

The stratigraphic architecture observed in the eastern and western sectors markedly differs from that described in the central part of the basin (where a well-organised succession of two fining-upward cycles is described), preventing a detailed correlation of the events across the basin. Also the relative abundance of facies in these three sectors of the basin is different: fine-grained sediments dominate in the central part, whereas coarser deposits occur to the west (Pizzo dei Tre Signori massif) and to the east (Lake Barbellino). The complex architecture of the basin, the difficulty in recognising events or trends that can be traced all across the basin and the different petrographic composition of conglomerates along the northern and southern margins of the basin suggest not only that tectonics controlled facies distribution and depositional environments but also the existence of sub-basins characterised by different evolutions within the greater Orobic Basin, further supporting the envisaged role of strike-slip tectonics.

#### **Recognition of Clastic Evaporites in the Catanzaro Trough, Calabria, South Italy**

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Keywords: Messinian salinity crisis, Re-Sedimented Lower Gypsum, Catanzaro Trough.

During second stage of Messinian Salinity Crisis (MSC) known as MSC acme (5.6-5.55 Ma) there was a tectonic pulse affecting the Maghrebian-Sicilian orogenic wedge followed by a rapid lowering of the sea level. This caused exposes of the Primary Lower Gypsum (PLG), (Roveri et al., 2008) and subsequently theirs subaerial erosion with formation of clastic evaporites facies called Re-Sedimented Lower Gypsum (RLG). Along the northeastern side of the Catanzaro Through (CT - Calabria, South Italy), crop out clastic units, containing gypsum clasts/blocks, which can be related to RLG. In detail, close to Marcellinara gypsum quarry outcrop a lithostratigraphic unit made by blocks and slumps of massive and giant gypsum facies with a politic matrix. This chaotic unit recorded the acme of MSC and represent a peculiar facies of the Maghrebian-Sicilian orogenic wedge (Roveri et al., 2008) and of the Crotone and Rossano Basins (Barone et al., 2008). Moving toward the inner side of the Basin, we observe a lithostratigraphic unit made up by dark-grey pelites interbedded with arenaceous bodies and conglomerates including. In the arenaceous bodies are sometimes present rip-up mud clasts, clay chips, ripples, and flames structures. The conglomerates are massive and include clasts of primary and clastic gypsum and of igneous-metamorphic rocks. Toward the sedimentary succession top, is present a thick lithostratigraphic unit consisting of an association of conglomeratic and arenaceous facies with a fining and thinning upward trend. At the unit bottom, prevail the facies related to massive sedimentary process, while toward the top increase the organized and channelized bodies. In this unit we observe clasts and blocks (up to 2m) of primary gyspsum (massive and branching selenite) which decrease toward the unit top.

The comparison between the stratigraphic scheme of RLG of the CT and the stratigraphic-depositional model refined by Roveri et al. (2008) for the foreland basin system of the middle-western Mediterranean Sea highlights the presence of a chaotic and massive body due to the re-sedimentation of the PLG evolving toward a siliciclastic sedimentation.

A more detailed study of clastic evaporates of the CT is important in order to create model of basin evolution and for interpreting the past record of such critical events that led them to form.

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# First account on some tritorial teeth from the Upper Jurassic of Mt. Nerone pelagic carbonate platform: paleoecological implications

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Keywords: Ginglymodian fishes, Umbria-Marche-Sabina Domain, Jurassic PCP-basin system.

By the early nineteenth century, the pelagic carbonate platform (PCP) of Mt. Nerone in the Umbria-Marche Sabina (UMS) Domain (Umbria-Marche Apennine, Italy) attracted scholars from all over Europe due to the wealth of fossil fauna preserved in a stunningly well-exposed Mesozoic sedimentary succession. Several geo-paleontological studies were focused on the abundant and diverse invertebrate fauna, while contributions dealing with Mesozoic fossil vertebrate were to date virtually lacking. Recently, the first material referable to hybodont sharks, consisting of an articulated crushing dentition, was described from the area and referred to as Asteracanthus cf. A. magnus. In this contribution, we report the first evidence of ginglymodians actinopterygians from the Upper Jurassic of Monte Nerone. The material is represented by seven highly tritorial isolated teeth collected from three classic localities of the area (i.e. Pian del Sasso, Fosso Pisciarello, I Ranchi). The general morphology of the material under study allow us to tentatively refer the teeth to as ?Scheenstia sp., a ginglymodian lepisosteiformes fish with a Late Jurassic (Kimmeridgian) to Early Cretaceous (Hauterivian-Barremian) distribution. The occurrence of durophagous organisms, to date represented by hybodont sharks and lepisosteiformes fishes, reveals interesting palaeoecological scenarios characterizing the PCP-basin system of Mt. Nerone, which were most likely triggered by large-scale geodynamic processes. The complex submarine palaeotopography, inherited by the Early Jurassic rifting phase, aroused the establishment of new infaunal and epifaunal communities in relatively deep (up to 150 m below sea-level) pelagic settings, opening up unexplored trophic niches for durophagous predators. The peculiar geodynamic setting of the UMS Domain, consisting of predominantly interconnected structural highs and lows, and the relative evolution of a diverse invertebrate fauna characterized by terebratulid, ostreids, limids, brachiopods, crustaceans and gastropods, attracted both hybodontids and durophagous ginglymodians in the Tethyan Realm, influencing their dispersal during the Late Jurassic.

## The Calabrian evaporite deposits: insights into selenite and halite genesis during the Messinian Salinity Crisis

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Keywords: Messinian salinity crisis, Gypsum, Halite.

During Late Miocene (~6Ma), the Mediterranean underwent a progressive restriction of oceanic water circulation known as the Messinian Salinity Crisis (MSC). This event, triggered the formation of extensive selenite and halite bearing evaporite deposits known as the Lower and Upper Evaporites (Rouchy and Caruso, 2006). These deposits have been studied on a regional scale (e.g. Spain, Central-Northern Italy, Sicily). However, the selenite and halite evaporites occurring in Calabria have not been studied in detail. Selenite outcrops are restricted to two disused quarries, one close to Marcellinara (Catanzaro province), the other in Benestare (Reggio Calabria province). Marcellinara's selenite displays swallow tail twinning (Cianflone et al., 2012). Halite salt dome deposits outcrop in the central-northern Calabria region (i.e. Verzino, Zinga, Coste del Sale, Lungro) and show macro and microcrystalline structures (Schreiber et al., 2007).

Petrographic and fluid inclusion (FI) studies of giant Marcellinara selenite crystals are used to investigate the palaeo-climate and palaeoenvironment present during the evolution of the deposit. Field and petrographic studies reveal the presence of three selenite facies: facies A, composed of giant selenite, facies B comprises banded selenite and facies C characterized by curvilinear massive selenite. Petrographic studies reveal the presence of alternating growth intervals in the selenite crystals that are occasionally separated by transition zones.

The degree of recrystallization of halite from several salt domes in the Crotone Basin is also investigated. Crystals have a mosaic texture, are sub-millimetric to millimetric in size, display prismatic habits and were oriented parallel to the water surface. The presence of relict primary crystallization features that have survived burying events are observed. FIs are monophase liquid, two-phase liquid-rich and multiphase solid-rich with occasional organic matter trapped within. UV Light Microscopy was used to determine the nature of the organic matter and to confirm the occurrence of prokaryotes and eukaryotes. Their presence reflects the lack of deformation during burial. This study helps to place the Calabrian evaporite deposits into the interpretive framework of the MSC.

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# Tetrapod tracks from the Vera Formation (Los Menucos Group, Río Negro province, Argentina) and their bearing on the chronostratigraphy of the Los Menucos Basin

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Keywords: Dicynodontipus, Pentasauropus, Triassic.

The Los Menucos locality, in the north-western sector of the North Patagonian Massif (Río Negro province, Argentina), hosts a volcaniclastic succession mainly composed of dacitic to rhyolitic ignimbrites, mesosilicic lavas and subordinate sedimentary rocks made up mainly of sandstones, all pertaining to the Los Menucos Group. Within the Los Menucos Group are included two units of lower rank, namely the Vera Formation and the Sierra Colorada Formation. The Vera Formation is notable for having produced one of the most important Triassic tetrapod ichnofauna of southern South America (e.g. Melchor & de Valais, 2006 and references therein). The ichnofauna, preserved both in volcaniclastic and sedimentary strata, is mostly documented both by small and large pentadactyl tetrapod tracks. These footprints are referred to the ichnogenera Dicynodontipus and *Pentasauropus*, respectively, and can be attributed to different therapsid trackmakers. The track-bearing levels from which *Dicynodontipus* and *Pentasauropus* were reported are exposed in two distinct areas, respectively to the west and east of the Los Menucos town. A Late Triassic age was historically proposed for the Los Menucos Group, based on palaeofloristic and palaeoichnological data, available from the Vera Formation, and radiometric datations available from the Sierra Colorada Formation. Recently, new geochronological evidence (Luppo et al., 2017) indicated ages ranging from the Wuchiapingian (Late Permian) to the Olenekian (Early Triassic) for the volcanics of Los Menucos Group, strongly contrasting with the current chronostratigraphical framework. Within this context, the ichnological record turn out to be binding for assessing the age of the sedimentary and volcaniclastic levels and estimating the starting of sedimentation in the Los Menucos Basin. The Late Triassic age for the whole Vera Formation can be questioned taking into account the global stratigraphical distribution of Dicynodontipus, spanning from the Late Permian to the early Middle Triassic (e.g. Klein & Lucas, 2010). Thus, while the *Pentasauropus*-bearing strata can be confidently referred to a Late Triassic age based on the global occurrence of the ichnogenus, sedimentary levels with *Dicynodontipus*, stratigraphically close to the dated volcanites, can be anticipated to Late Permian or Early Triassic times.

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## First tetrapod footprints from the Permian of Sardinia

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Keywords: Italy, Merifontichnus, Permian.

The Torre del Porticciolo palaeontological locality (Alghero, N-W Sardinia, Italy) returned the skeletal remains of the first Permian basal synapsid from Italy, Alierasaurus ronchii (Romano & Nicosia, 2014, 2015; Romano et al., 2017), the largest late early Permian to early middle Permian non-therapsid synapsid known to date. Recently, other skeletal remains preliminarily attributed to a carnivorous non-therapsid synapsid were described from a second site, approximately from the same stratigraphic level within the Cala del Vino Fm. (Romano et al., 2018) and tetrapod tracks were found at a third site. This last finding represents the first ichnological record from the Permian of Sardinia. The general morphology of manus and pes tracks, the relative proportions and the position of digit I, enabled referring the new material to as *Merifontichnus*, an ichnotaxon established from the uppermost portion (La Lieude Fm.) of Permian succession of the Lodève Basin (south France). Footprint dimensions, ranging between 4 cm and 10 cm in length, indicate two trackmakers of different body size, respectively of about 50 and about 100 cm in total length. The Cala del Vino Fm. turns out to be one of the few examples in the Permian of Europe of combined ichno- and body-fossil record. The two source of data, once integrated, provide different representations of the faunal composition, enhancing the understanding of the faunal diversity of this area of Pangea during the latest early Permian to early middle Permian time interval. While the skeletal remains indicated medium-to large carnivorous basal synapsids and giant herbivorous caseid (i.e. Alierasaurus ronchii), the recently discovered ichnosite adds as further constituent of the terrestrial palaeofauna also a small animal represented by Merifontichnus trackmakers. The occurrence of this ichnotaxon from Italy allowed to confirm the early middle Permian age of the Cala del Vino Fm. The new material is the first reliable occurrence of Merifontichnus from Italy. Moreover, it represents to date an anticipation of the occurrence if compared to the alleged age of the La Lieude Fm., where Merifontichnus was established.

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# The effects of orbital forcing archived in a sedimentary succession across the onset of the Messinian salinity crisis

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Keywords: Orbital forcing, Messinian salinity crisis, Major and trace elements.

In marginal Mediterranean sub-basins, the early phase of the Messinian salinity crisis (MSC) is recorded by cyclic successions of gypsum and shales, which in deeper parts of the sub-basins make lateral transition into organic-rich shales, marls, and carbonates. The cyclic stacking pattern of the gypsum-bearing sequences is believed to reflect precession-driven climate change, based on the assumption that shales reflect humid climate (precession minima) and gypsum arid conditions (precession maxima). However, this correlation has not been verified to date, mostly because of the scarcity of microfossils, which represent the most common tools for the reconstruction of orbitally-driven paleoclimate perturbations. Such perturbations can instead be reconstructed through the study of the deeper water counterparts of gypsum with geochemical indicators (major and trace elements, lipid biomarkers), which provide insight on climate and aquatic productivity. We used this approach for the study of an astronomically-tuned section from the Piedmont Basin (NW Italy) in which the onset of the MSC is archived in a sequence of organic-rich sediments. This sequence displays distinct lithological cyclicity, evidenced by the repetition of couplets of organic-rich shales and marls, both either bioturbated (in the pre-MSC part of the section) or laminated (in the MSC part). The influence of orbitally-driven (precession) climate oscillations is demonstrated by fluctuations of Ti/Al, Si/Al, Mg/Al, K/Al, Zr/Al, Ba/Al ratios that are in phase with lithological cyclicity. These fluctuations are interpreted to reflect alternation of humid (shales, reflecting precession minima) and arid (bioturbated and laminated marls, reflecting precession maxima) phases, dominated by fluvial and aeolian transport of detrital material, respectively. The cyclicity of the element ratios is mirrored by changes in organic carbon content and biomarker inventory. In particular, the distribution of long-chain *n*-alkanes and their degree of preservation reveal that humid phases at times of precession minima were typified by the maximum input of degraded terrestrial organic matter driven by enhanced riverine runoff, which promoted water column stratification. Coeval increase in Ba content, a common paleoproductivity proxy, agrees with enhanced nutrient supply during humid periods, promoting phases of eutrophication in the basin. Lithological and geochemical changes are observed in MSC sediments deposited at times of precession maxima, evidenced by the replacement of pre-MSC bioturbated marls by laminated marls rich in filamentous fossils corresponding to the remains of probable colorless sulfide-oxidizing bacteria. Such changes reflect an intensification of water column stratification after the onset of the MSC, possibly related to the combined effects of persistent freshwater inflow and basin isolation, preluding the advent of gypsum precipitation.

### The "Abbeveratoio" Section: a peculiar Toarcian succession in the central Apennines

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Keywords: Toarcian, ammonite biostratigraphy, facies analysis.

The "Abbeveratoio" stratigraphic section crops out close to the top of Monte La Pelosa (Terni, Umbria, Italy). Its deposits were dated to the Toarcian-Bajocian interval by means of ammonite biostratigraphy, but its sedimentological features are clearly different from those observed in most of coeval succession, at least as far as the Toarcian is concerned.

The lower part of the succession, dated to the upper Serpentinus to Variabilis ammonite zones (Di Cencio, 2007) is characterized by the Monte Serrone Marls (Pialli, 1969), a sequence of gray and calcareous marls, thinly bedded, sometimes with calcareous nodules. In the lower part mainly, some calcareous levels can be observed. They are made of cemented and alternated oolitic and bioclastic limestones. The alternation between red and green levels, corresponds to oolitic and bioclastic intervals.

The top of the lower succession is characterized by the occurrence of sandy plagues rich in brachiopods and benthic foraminifers, such as *Agerina martana* (Farinacci, 1959). The occurrence of this marker of the Pliensbachian, suggests that these layers were reworked and slided down onto the Toarcian sea bottom.

The upper part of the section, dated to the Speciosum to Murchisonae Zones (Upper Toarcian, lower Aalenian), is markedly different and is made mainly by thick layers of calcareous Rosso Ammonitico.

Upward the succession is characterized essentially by re-deposited levels that are more numerous than autochthones ones. The biostratigraphical analysis was carried out with ammonites found in the autochthonous layers, even though numerous fossils were discovered also in the reworked beds.

In these latter layers fossils are eroded and randomly distributed.

The reworked layers show a typical turbiditic features in which the Bouma Sequence (Bouma, 1962) can be identified. Fining and thinning upward sequence and cherty levels are also observable.

The finding of fossils within the reworked beds suggests the continuous erosion of a structural high that locally nourished the deposition of turbidites and debris flow deposits, in a narrow PCP system (*sensu* Santantonio, 1994).

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# The Upper Turonian-Santonian neritic carbonates in the northern Simbruini Mts. (Central Apennines, Italy): integrated stratigraphy and palaeoecological considerations

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Keywords: Cretaceous, Carbonate platform, Benthic forams.

Five Upper Cretaceous stratigraphic sections have been measured and sampled in the tectonically complex area of Marsia (northern Simbruini Mts.), allowing the reconstruction of a ~60 m thick inner carbonate platform succession.

The section begins with thin bedded dolomitized limestone with Discorbidae, Miliolidae and ostracoda, passing upwards to decimeter-thick wacke-to-packstone limestone with rudist fragments and *Nezzazatinella* cf. *aegyptiaca*. Metre-thick rudist float-to-rudstones follow upwards, with *in situ* assemblages dominated by elongate shells of *Radiolites trigeri*, occurring both in monospecific levels or associated with *Durania arnaudi* and *Biradiolites angulosus*. Microfacies are composed of *Moncharmontia* cf. *compressa, Nummuloculina* cf. *irregularis, Spirosigmoilina rajkae* and Rotaliidae. Upwards, a stack of thick-bedded limestone with float-to-rudstone texture occurs, at first characterized by a *Biradiolites martellii* oligospecific association, evolving in more differentiated rudist assemblages, composed of *Sauvagesia* sp., *B. martellii, Lapeirousella samnitica* and rare *Vaccinites* sp. Sparse bioclastic lenses with nerineids also occur. The associated microfacies is composed of *Dicyclina schlumbergeri, M. compressa, Nezzazatinella picardi, Pseudocyclammina sphaeroidea, Nummoloculina* sp., *Rotorbinella scarsellai*.

The overlying succession is a ~ 45 m thick stack of whitish limestone with floatstone to rudstone texture, containing benthic organisms such as *Accordiella conica, Scandonea samnitica, S. mediterranea, Decastronema barattoloi, Tetraminouxia salentina, Calcarinella schaubi, R. scarsellai, Murgeina apula and Reticulinella fleuryi.* Macrofossil assemblages are dominated by rudists, occurring in floatstones with *Hippurites sulcatus, Vaccinites fortisi, Plagioptychus paradoxus, Radiolites* cf. *dario,* along with rare massive corals. Significantly, sparse floatstones characterized by whole regular echinoids occur, and a peculiar horizon is characterized by abundant calcareous sponges (Chaetetids). This testify a heterogeneity of facies and possible perturbations in sea-water circulation, in turn fostering the proliferation of rudists, chaetetids and/or echinoids. Remarkably ~10 m below the top of the section the uppermost Santonian *Keramosphaerina tergestina* horizon occurs.

The composed succession can be referred to the "*N*. cf. *aegyptiaca* and *N*. cf. *irregularis*" and "*A*. *conica* and *R*. *scarsellai*" biozones, encompassing the late Turonian- uppermost Santonian interval.

The section has been reconstructed despite the structural complexity of the area and is only  $\sim 60$  m thick, resulting very thin if compared with other coeval succession as the S. Maria dei Bisognosi section ( $\sim 10$  km E of Marsia), where the Coniacian-Santonian is  $\geq 200$  m-thick. Such significant difference can be explained envisaging tectonic activity that produced different rates of accommodation space creation during the late Cretaceous, eventually coupled with outcrop exposure.

# A 9 million-year-long astrochronological record of the early-middle Eocene corroborated by seafloor spreading rates

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Keywords: early-middle Eocene, Umbria-Marche basin, integrated stratigraphy.

The early-middle Eocene (~56-41 Ma) is recorded in the pelagic Scaglia Rossa and Variegata Formations of the Umbria-Marche basin (central Italy). Geochemical and magnetostratigraphic alignment between the Bottaccione section (Gubbio, central Italy) and the Smirra core (Cagli, central Italy) allow us to generate a continuous and well-preserved new record that, combined with previously published data from the same area (Galeotti et al., 2010, 2017), creates a continuous high-resolution record from the Paleocene-Eocene Thermal Maximum (~56 Ma) to the lower part of Chron C21n. Comparison with carbon isotope records from ODP Sites 1258 at Demerara Rise and ODP Site 1263 at Walvis Ridge reveals a satisfactory match, providing further evidence of the global significance of the long-term trend and superposed perturbations captured by the  $\delta^{13}$ C records. The identification of orbitally forced geochemical cycles allow us to develop a 405-kyr tuned age model, thereby extending the astrochronology for these classic Tethyan successions from  $\sim$ 56.0 to  $\sim$ 47.5 Ma. Marine magnetic anomaly profiles from major oceanic basins characterized by high seafloor spreading rates are used to independently test the astronomical polarity time scale associated with our tuning as well as other polarity time scales. Our age model suggests the existence of periods of relatively constant seafloor spreading rates separated by rapid changes, while the other time scales generate more gradual variations and also include large and short-term deviations in spreading rates that occur simultaneously in different oceanic basins, implying errors in polarity reversal ages. Refining the timing of these spreading rate changes is very important as it may help determine the causative mechanism for these changes, especially around  $\sim 50$  Ma which is a period of worldwide changes in the seafloor spreading and also coincides with the beginning of a long-term decrease in the temperatures and pCO<sub>2</sub>.

We therefore conclude that Umbria-Marche basin records provide a valuable cyclochronological and astrochronological estimate for the duration of the interval between  $\sim$ 56 to  $\sim$ 47 Ma. The new age model further contributes to the closure of the middle Eocene gap in the Astrochronological Time Scale.

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# Microbialite within oxygen-depleted cavities: geomicrobiological laboratories to decipher ancient environment perturbations

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Keywords: microbialites, bioconstructions, anoxic cavities.

Stressed conditions are ideal for the development of microbial communities. Bioconstructions are made of a complex skeletal network with millimetric to centimetric primary cavities where decaying organic matter create oxygen-minimum zones. Autotrotrophic and chemoheterotrophic bacteria can grow in these cryptic niches inducing, with their metabolic activities, biomineralization processes. Mediterranean submarine caves hold one of the best examples for studying microbialites which thrive in cryptic environments, and they also allow to compare these recent microbialites with their fossil counterparts. Here we compare the microbialites growing inside small biostalactites of recent submarine caves with those developed within the Triassic patch reefs of Dolomites (Russo et al., 1991). The microbial-induced biomineralization is the consequence of autotrophic and chemoheterotrophic bacterial activities in both systems (Guido et al., 2013; Tosti et al., 2011). Sulfate Reducing Bacteria (SRB), fed by the organic matter produced by metazoans, flourish in suboxic cavities of the skeletal framework, and induce autochthonous micrite deposition and the early stabilization of the bioconstructions. The *in situ* characterization of organic matter through Raman spectroscopy allowed to record similar organic G and D bands for the autochthonous micrite of both bioconstructions. These peaks correspond to disordered Carbonaceous Material (CM) preserved in the microbialites. CM bands were not identified in the allochthonous micrite. Raman data strengthen the hypothesis of an analogous SRB mediation for the microbialite deposited in cryptic niches of the recent submarine caves and Triassic patch reefs. The comparison with published extract-based studies (GC-MS) corroborates this hypothesis since distinctive biosignatures of SRB have been identified in the microbialite phases of both the bioconstructions. Stressed conditions can develop at different scale, environments and geological time, therefore the framework cavities of the bioconstructions can be considered laboratories to study microbial induced mineralization in oxygendepleted environments.

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# The potential role of internal waves on mesophotic coral facies developments: the case study from Iran and Italy (Late Oligocene)

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Keywords: Late Oligocene, mesophotic corals, internal waves.

During the late Oligocene coral facies, usually associated with Larger Benthic Foraminifers, become widespread in many carbonate systems all around the World (Perrin, 2002; Hallock et al., 2006). Outcrops from Oligo- Miocene Asmari Formation (Zagros basin, Iran) and Grotta San Michele Limestones (Gargano, southern Italy) has been studied in order to document the type and distribution of carbonate facies and then to analyze the controlling factors of the development of carbonate factories. The Grotta San Michele Limestones were deposited during the late Chattian to the Aquitanian; Asmari Formation span in age from the Rupelian to the Burdigalian.

The Grotta San Michele Lms. is a massive unit characterized by the presence of scattered coral colonies, or fragments in a wackestone to packstone matrix. The other common components are red algae, larger benthic foraminifers (mostly rotalids), epiphytic foraminifers and gastropods. In the Asmari Formation, the middle-upper Chattian interval is represented by Coral facies that forms limited buildups, developed in open shelves setting (ie. mid-ramp). The corals are accompanied with non-articulate coralline algae fragments, small benthic foraminifers and small fragments of LBF.

The upper Oligocene corals facies and its associated skeletal grains in both Grotta San Michele Lms and Asmari Fm occur in a fine-grained, muddy matrix, and were not able to build a rigid framework, which fits them to the cluster reef type. All these characteristics are here interpreted as the result of the deposition below the wave-base action and in a mesophotic condition. Some requirements of corals such as food supply and water movements, in low- energy mesophotic setting, can be related to the internal waves action (Morsilli et al., 2012; Pomar et al., 2017). Internal waves/tides are an effective and well-documented mechanism to displace nutrient- rich water and create turbulence and currents in a generally quiet environment (Pomar et al., 2012).

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# Calcareous microfossils size decrease at the beginning of the Messinian salinity crisis: data from the Piedmont Basin

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Keywords: Messinian Salinity Crisis, calcareous plankton, dwarfism.

The Messinian salinity crisis (MSC) is a short lived (5.97-5.33 Ma) dramatic paleo-oceanographic event occurred in the Mediterranean area as result o reduced hydrological connection with the Atlantic ocean. The beginning of the MSC, marked by the deposition of gypsum in the marginal basins, triggered an immediate response of the biota, and particularly of the calcareous microfossils. In detail, the first 21 kyr of the crisis were characterized by very peculiar calcareous nannofossil and foraminiferal assemblages preserved in the first Primary Lower Gypsum (PLG) cycle (*Sphenolithus abies*, *Umbilicosphaera rotula*, and *Rhabdosphaera procera* peaks, *Globorotalia scitula* and *G. suterae* peaks; Lozar et al. in press). Also, in the lower PLG cycles some foraminiferal taxa exhibit a sharp size decrease (e.g. *Turborotalita quinqueloba*), ), the significance of which is still unclear. In addition, no information regarding the size of the calcareous nannofossils is available so far.

Samples from the Piedmont Basin (northern Italy) and straddling the MSC onset yielded the *Sphenolithus abies* and *Helicosphara carteri* specimens measured for this work. Total length and basal width for *S. abies* and major and minor axes for *H. carteri* specimens were measured. The measures sharply decrease at the onset of the MSC but show a slow recovery to average values in the following cycles, despite their group abundance decrease.

As for other calcareous microfossils, among the foraminiferal assemblages from the same cycles, the >125 micron fraction is devoid of foraminifers, whereas the 45-63 micron and 63-125 micron fractions contain abundant *Turborotalita quinqueloba* and minor *Bulimina* spp., thus showing a sudden size decrease in the cycle where most foraminiferal taxa abruptly disappear. The disappearance of foraminifers and nannofossils at the beginning of the crisis was traditionally related to a fast salinity increase, in turn responsible for the deposition of the evaporites recorded in the marginal basins of the Mediterranean Sea. Conversely, the size decrease among calcareous nannofossils and foraminifers described in this study suggest that the surface water was characterized by high nutrient supply and possibly fresh water input. The eutrophication is also supported by the presence of *Umbilicosphaera* spp. blooms, a calcareous nannofossil genus considered to better flourish when nutrient supply is high, by the presence of diatom frustules, and by other independent geochemical data (e.g. high Ba concentration).

The assemblage composition and the microfossil size decrease recorded in this study thus suggest that the MSC could have been triggered by high nutrient input to the basin, possibly derived by increased runoff from the continent.

# Calcareous Nannofossils and foraminifer Mg/Ca record: new paleoenvironmental and biostratigraphic insights at and prior to the onset of the Messinian salinity crisis in the Sorbas Basin

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Keywords: Messinian salinity crisis, Coccolithophores, Mg/Ca Orbulina universa.

Since the evaporites were discovered on the Mediterranean floor, an intense debate has arisen about the most appropriate scenario for the onset of their deposition, occurring at about 5.97 Ma. The Sorbas Basin (SE Spain) records a continuous and complete succession of events characterizing the Messinian salinity crisis (MSC). We focus on the astronomically tuned pre-evaporitic Upper Abad Mb. (UA) and the lowermost Primary lower gypsum deposits (PLG). The UA deposits are characterized by a well-defined precession-driven lithological cyclicity, commonly made up of quadripartite cycles (sapropel - marl - diatomite - marl). The PLG unit represents the evaporitic phase and is composed of shales - gypsum cycles. Samples were collected in the Perales section (cycles UA23 to UA34) and in the shales of the lowermost 4 PLG cycles. Calcareous nannofossils (CN) relative abundance and Mg/Ca on the foraminiferal shells of Orbulina universa (only in the UA) are measured in order to obtain information about the environmental condition leading to the gypsum deposition, usually interpreted as a change (increase) in salinity. These data could also help clarifying the disappearance of calcifying plankton, reported in many sections across the basin.

Preliminary results show that the CN are present throughout the studied interval, except in PLG1 and PLG2 shales. A peak in abundance of Sphenolithus abies, followed or accompanied by a peak of Helicosphaera carteri, Umbilicosphaera rotula and Rhabdosphaera procera has been identified in an interval approximating the MSC onset. The identification in the western Mediterranean of this peculiar succession of CN paleobioevents, previously reported in Italy (Sicily, Emilia Romagna and Piedmont) and Cyprus (Lozar et al., 2018 and references therein), strongly suggests that at approximately the time of the MSC onset, a strong increase in fresh water input and stratification of the water column affected the Mediterranean at basin-wide scale. This, at least in the Sorbas Basin, culminates in the alternate deposition of shale - gypsum cycles. By contrast, in the shales of PLG3 and PLG4 cycles the CN assemblage reflects almost normal marine conditions with high productivity in the water column, suggested by the quasi monospecific assemblage comprised by Reticulofenestra spp and Coccolithus pelagicus.

Summarizing, we report the first continuous CN record at the time and before the MSC in the Sorbas Basin. The finding of the CN paleobioevent in the Western Mediterranean strongly suggests that the evaporitic stage was triggered by the same changes in all the Mediterranean basins, which points to a high fresh water input and stratification of the water column events.

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# Coccoliths, CO<sub>2</sub>, Sapropels and Climate: clues from a core in the Ionian Sea

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Keywords: Coccolithophores, Sapropel S1, Climate change.

A high-resolution abundance and biometrical Coccolithophore study is performed in core M25/4-12 (Ionian Sea) containing the sapropel S1. By comparison of these data to  $\delta^{18}$ O, the main climatic events characterizing this period have been recognized, such as the Last Glacial Maximum, the Younger Dryas and the Max Monsoon. Some clues can be depicted after the study of the assemblage. In fact an important feature reported in literature is the correlation existing among the five younger sapropel (S1-S5) deposition and the increase in atmospheric  $CO_2$  content (Negri et al., 2012). The authors hypothesized a local response of the systems to carbon removal from the oceanic water masses during the interglacial periods. According to the literature, coccoliths account for 10% of phytoplankton biomass and the shift observed in the assemblage characterizing S1 indicate that across this layer 90% of the assemblage consisted of *Emiliania huxleyi*. Mesocosm study demonstrated that this specie is furthermore able to secrete Trasparent Exopolymers Particles (TEP), and as all the forms characterized by a calcareous test can promote the so-called Ballast effect. We suggest that the combinate effect of enhanced TEP production increasing the aggregation of organic carbon, the CaCO, platelets protecting from organic matter degradation and the ballast function for the organic matter sinking were crucial for the S1 formation. This based on model studies by Klaas and Archer, 2002 suggesting that a 33% increase in organic matter is sufficient to draw down the CO<sub>2</sub> in the seawater by approximately 60 ppm. Then, Coccolithophore possibly played a key role in this process and in agreement with the Gaia hypothesis (Lovelock 1979), and when the atmospheric  $CO_2$  level increased, the biotic component of the ecosystem attenuated the effects sequestering organic carbon (Sapropel) in the sediment whose fate otherwise was to reenter in the global carbon cycle.

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Lovelock, J.E. (1979): Gaia. A new look at life on earth. Oxford University Press, Oxford McIntyre

Negri, A., Colleoni, F. & Masina, S. (2012): Mediterranean sapropels: a mere geological problem or a research for study of a changing planet?. Alpine and Mediterranean Quaternary, 25, 2, 81-89.

# Planktonic assemblage variability during the deposition of sapropel S5 in the Ionian Sea

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Keywords: Sapropel S5, microfossils, tephrochronology.

Sapropels are distinctive dark sediment layers occurring periodically in the Eastern Mediterranean Sea during the late Neogene, caused by enhanced primary productivity and/or deep-water stagnation. Every sapropel shows peculiar features, likely related to different climate forcing, hydrological parameters and response to productivity and preservation. Here, we report the results from Sapropel S5 of core M25/4-12, collected in the Ionian Sea, which records the last 10 sapropels. Sapropel S5, deposited shortly after the end of Termination TII, is one of the best-developed sapropels. Investigation of planktonic foraminiferal and dinocyst assemblages, together with stable isotope analyses, provides insight into the climatic and oceanographical changes across this event. High-quality age control is based on a high-resolution biostratigraphic framework validated with a detailed tephrochronological study. Three volcanic levels were recorded below and intercalated in S5. Petrography allowed identifying a rhyolitic volcanic layer corresponding to a Pantellerite in the presapropel oxidized sediments (dated 131 ka) and two tephra levels (C-36 and C-35) were identified and dated at 123 ka and 121.5 ka, respectively.

The planktonic assemblages indicate that milder conditions and an increase of productivity in the water column started at about 3 ka before the beginning of sapropel deposition. Warmer surface waters and stratified conditions marked the onset of the deposition of the sapropel. After one thousand year, stronger seasonal contrast due to colder winters started and persisted for about 3.5 ka. The last interval of the sapropel deposition, which lasted about 2.5 ka, is marked by warmer surface water and intense stratification with a well- developed deep chlorophyll maximum. The termination of sapropel deposition, determined on the basis of the dark sediment colour, corresponds to an important increase of herbivorous planktonic foraminiferal density, which could suggest a further pulse of primary productivity.

# Late Miocene (Messinian) marine carbon cycle perturbations recorded by positive $\delta^{13}$ c excursion of molecular fossils in a semi-enclosed Mediterranean Subbasin (Piedmont basin)

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Keywords: Carbon cycle, molecular fossils, Messinian salinity crisis.

Carbon cycle perturbations have been common in the geological past, and their effect on sedimentary sequences is recorded by negative and positive carbon isotope excursions. Semi-enclosed basins, such as the Mediterranean Sea, are excellent natural laboratories to investigate ancient carbon cycle perturbations and their impact on ecological change. The amplitude of these perturbations is mirrored by the magnitude of isotope fluctuations affecting different carbon sources, including carbon from different pools that becomes incorporated in biogenic and authigenic carbonate minerals and organic matter.

Unfortunately,  $\delta^{13}$ C values of carbonates and organic matter can be overprinted to different degrees by diagenesis. To minimize this problem, we investigated carbon stable isotopic signals of carbonate, bulk organic matter, and molecular fossils preserved in fine-grained sediments (shales and marls) that were deposited in a semi-closed Mediterranean basin (Piedmont Basin) during the Messinian salinity crisis (MSC). So far, the disappearance of body fossils (especially calcareous plankton) at the advent of this dramatic event hampered reliable paleoenvironmental reconstructions. However, molecular fossils including glycerol dibiphytanyl glycerol tetraethers (GDGTs) sourced by marine planktic Thaumarchaeota (crenarchaeol and other GDGTs) are found in all MSC sediments. Interestingly, crenarchaeol records a positive carbon isotope excursion above the MSC onset (from an average of -21% PDB in the pre-MSC sediments to values as high as -16% PDB in the MSC sediments). Since planktic Thaumarchaeota are thought to primarily fix carbon by assimilation of dissolved inorganic carbon (DIC) and fractionation factors are known from one experiment with cultured planktic Thaumarchaeota, the  $\delta^{13}$ C values of crenarchaeol can be used to calculate the paleo- $\delta^{13}C_{DIC}$  of Messinian waters. Our results indicate that  $\delta^{13}C_{DIC}$  values were similar to modern values in pre-MSC times ( $\delta^{13}C_{DIC} : -0\%$ ). In contrast, during the MSC  $\delta^{13}C_{DIC}$  values increased, reflecting a so far unexplored positive carbon isotope excursion (+4‰) and suggesting that environmental and ecological change at the advent of the MSC was significant. These data show that carbon isotope analyses of different carbon pools are a powerful tool to unravel paleoenvironmental change.

# The sapropel theme: DSDP, ODP and beyond

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Keywords: Sapropel, Paleoceanography, Paleoclimatology.

Sapropels are sediments rich in organic carbon occurring cyclically in the Mediterranean marine records and whose origin has been matter of great debate during the last decades.

Since the very beginning of the history of studies on sapropels, authors inferred that those levels, interbedded as dark layers in more or less normal light "open marine" sediments, formed during short-lived but catastrophic alterations in Mediterranean oceanographic conditions, probably linked to broader climate changes.During DSDP leg 13 and 42 cores conatining sapropels were raised and later ODP legs 160 and 161 permitted to recognize 88 sapropels spanning the Plio-Pleistocene time interval. I will summarize the main results after the DSDP-ODP legs in the Mediterranean and outline possible new applications in the study of these mysterious sediments.

### Microbial reefs revived - the impact of paleoenvironmental perturbations on reefal ecosystems

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Keywords: reefal microbialites, end-Permian mass extinction, Holocene.

Following the dominance of microbial carbonate in reefal ecosystems in the Precambrian, the Phanerozoic saw an overall decline of microbialites in reefs. Different metazoans formed reef frameworks in the course of the Phanerozoic, commonly with major changes in communities after mass extinctions. In the aftermath of some major crises, microbial carbonate production regained importance and microbialites even supported the framework of reefs in some instances. In order to better understand the uneven distribution of reefal microbialites in the Phanerozoic, the factors constraining their formation need to be identified. Among these, (1) metazoan competition - particularly grazing - and (2) seawater saturation state in respect to calcium carbonate minerals have been suggested to be critical (Riding, 2005). To assess the significance of seawater alkalinity, the actual mechanisms of microbial carbonate formation need to be identified. Should the formation of reefal microbialites be largely driven the mineralization of extracellular polymeric substances (EPS), seawater alkalinity will indeed be a crucial factor. Should microbialite formation, however, result mostly from metabolic activity, the effect of seawater alkalinity will be less significant.

Here, I will look into two examples of microbial carbonate production in reef settings - microbial bioherms that formed after the end-Permian mass extinction and Holocene reefal microbialites. Recent work revealed that the earliest Triassic reef ecosystems were surprisingly diverse and that keratose sponges were a previously unidentified component in framework building. The associated microbialites formed from microbial mats that were apparently dominated by cyanobacteria but also contained anoxygenic phototrophs and sulfate-reducing bacteria, closely resembling the composition of extant photosynthesis-based microbial mats. In sharp contrast to this, Holocene reefal microbialites lack evidence for the involvement of phototrophic microorganisms in their formation. These microbial carbonates only reveal biosignatures of heterotrophic bacteria. Carbon stable isotope patterns suggest that neither phototrophy in case of Early Triassic microbial bioherms nor heterotrophy in case of Holocene reefal microbialite formation in reefal settings are variable, depending on environmental settings and interaction with framebuilding metazoans. No particular metabolism is apparently required for the formation of reefal microbialites and metabolic activity contributes less to carbonate production than EPS-controlled mineralization. Such relationship agrees with seawater saturation state as first and foremost control on the abundance of reefal microbialites in the Phanerozoic.

# Reconstructing high frequency paleoclimatic and paleoceanographic changes in the northernmost Mediterranean during the Late Miocene: insights from the diatomites of the Piedmont Basin

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Keywords: Piedmont Basin, Paleoceanography, Paleoclimatology.

In the latest Miocene, before the onset of the Messinian salinity crisis, the Mediterranean experienced a dramatic increase of the opaline production, resulting in the precessionally-controlled accumulation of laminated diatomites, sapropels and marls.

Previous studies on the Upper Miocene Mediterranean diatom-bearing successions were mostly focused on the characterization of their average composition, mostly through destructive analytical techniques based on the homogenization of the laminated sediment. Although this method provides useful information about the evolution of the diatom assemblage at *precessional* scale, it hampers a detailed reconstruction of the *subprecessional* (annual-to-seasonal) processes occurring in the water column and at the sediment-water interface. Such processes, driven by high-frequency climate change, can only be reconstructed through high-resolution analytical approaches based on the semi-quantitative investigation of single laminae through the scanning electron microscope, including backscatter imagery.

We applied such high-resolution analysis to the Upper Miocene diatomites of the Piedmont Basin (Pecetto di Valenza section, Monferrato), focusing on the processes operating at sub-precessional scale and responsible for the accumulation and preservation of these laminated sediments.

The identification and the characterization of sub-precessional sedimentary processes from coeval successions in the Mediterranean is crucial to assess the impact of paleoclimate on sedimentary sub-basins typified by different paleogeographic conditions and tectonic evolution.

# A microbial-dominated carbonate platform-to-slope system during the onset of the Messinian salinity crisis (Calcare di base Fm, southern Italy)

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Keywords: Microbial carbonate, Messinian Salinity Crisis, Carbonate Platform.

The Calcare di Base Formation (CdB) is the result of a widespread microbial-mediated carbonate deposition (Perri et al. 2017) occurring during the Lower Messinian in syn-orogenic basins, along the Calabrian and Sicilian accretionary wedges. The carbonates are associated with evaporites and are stratigraphically positioned at the onset of the Messinian Salinity Crisis, which culminates with massive salts deposition.

The formation of such extensive microbial deposition that largely comprises the CdB is envisaged to have taken place across shallow to moderate depth platforms, with slopes into deeper water areas where resedimentation occurred.

The most common inner platform sedimentary facies are stromatolites and thrombolites forming flat to low relief cm to m scale bodies. The micritic fabrics commonly preserve fossil bacteria, mainly filamentous, which implies an original microbial mat, probably dominated by sulphur-oxidizing bacteria (Thiotrichaceae); however, there is evidence for a more complex microbial community including sulphate- and/or nitrate-reducing bacteria, all being responsible for the mediation of the carbonate precipitation. Microbialitic boundstones are rich in pseudomorphs of Ca-sulphate and halite, which formed during the deposition of the carbonate. Layers of primary gypsum are interbedded locally with carbonates suggesting the presence of restricted hypersaline marine conditions.

While in situ microbialites growth and evaporites precipitation likely dominate at platform setting, gravity flows and ductile deformation prevail along the slopes, forming highly deformed shelf-derived blocks and debrites. A downslope facies gradient, developing along presumably gently inclined slopes, is observable from upper/mid-slope massive debrites to base-of-slope normal to reverse graded organized debrites; which, finally, make transition to basinal mudstones.

The prograding pattern of the platform-slope wedges show that the carbonates of the CdB form a continuous regressive sequence due to a progressive relative sea-level lowering.

The stable O and C isotopic composition of the carbonates, which varies from dolomite to aragonite and calcite, suggests alternation between arid to humid climatic changes, expressed by cyclic interbedding of carbonates and evaporites with marlstones.

Perri, E., Gindre-Chanu, L., Caruso, A., Cefala, M., Scopelliti, G. & Tucker, M. (2017): Microbial-mediated pre-salt carbonate deposition during the Messinian salinity crisis (Calcare di Base fm., Southern Italy). Mar. Petr. Geol., 88, 235-250.

# Environmental change across the onset of the Messinian salinity crisis recorded in deep water fine-grained siliciclastic sediments: the Govone section (NW Italy)

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Keywords: Messinian salinity crisis, water column stratification, GDGTs.

During the Messinian salinity crisis (MSC; 5.97-5.33 Ma) the progressive isolation of the Mediterranean Sea from the Atlantic Ocean led to the establishment of extreme environmental conditions, including hypersalinity, dysoxia and anoxia. Generally, in marginal shallow basins the advent of the MSC is marked by the deposition of primary massive gypsum. In contrast, gypsum was not formed in intermediate to deep basins, possibly due to severe bottom oxygen depletion, which favoured increased bacterial sulphate reduction, which in turn was responsible for gypsum undersaturation (de Lange and Krijgsman, 2010).

To look into the nature of environmental change in a deep-water setting across the onset of the MSC, we studied the Govone section (Piedmont Basin, NW Italy), a monotonous cyclical alternation of organicrich shales and homogeneous marls. Sedimentologic, petrographic and C and O stable isotope analyses were complemented by lipid biomarker analyses, focusing on the inventory of archaeal glycerol dialkyl glycerol tetraethers (GDGTs) and bacterial dialkyl glycerol ethers (DAGEs). Interestingly, predominantly GDGTs of marine planktic archaea (e.g. *crenarchaeol*) were found in both shales and marls before and after the MSC onset, indicating the persistence of normal marine conditions in the upper water column also after the begin of the crisis. The concomitant increase of DAGEs and spheroidal dolomite microcrystals in the MSC deposits is consistent with increasing rates of bacterial sulphate reduction and oxygen depletion in the bottom layers, the former probably at least in part responsible for gypsum undersaturation. Our lipid biomarker data confirm the presence of progressively more restricted conditions across the MSC onset, culminating with the establishment of a permanent stratification of the water column.

De Lange, G.J. & Krijgsman, W. (2010): Messinian salinity crisis: a novel unifying shallow gypsum/deep dolomite formation mechanism. Marine Geology, 275, 273-277.

### Can tephra deposition influence diatom assemblages in Antarctic marine sediments?

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#### Keywords: Ross Sea, Diatoms, Tephra.

Diatoms are very sensitive to minute changes in environmental conditions thus they represent an excellent proxy to understand how tephra influences environmental sedimentation. Some tephra layers have been recognized in cores collected in the framework of the PNRA-Project TRACERS (TephRochronology and mArker events for the correlation of natural archives in the Ross Sea, Antarctica) in the Western Ross Sea. We propose a study of the diatom assemblage on selected levels around primary tephra layers found in two piston cores collected in the northern Drygalski Basin (TR17\_05PC) and Wood Bay (TR17\_12PC). Core TR17\_05PC is characterized by sandy mud alternating with muddy sand. Two tephra layers are present. Core TR17\_12PC is characterized by clayey mud with sparse clasts. One tephra layer is present at the base of the core. Physical (magnetic susceptibility, grain size), chemical-geochemical (organic and total carbon, major and trace elements) and micropaleontological (foraminifera) analyses support the diatom assemblage.

Various authors (Telfold et al., 2004; Cruces et al., 2006; Urrutia et al., 2007) have demonstrated that tephra deposition modifies the chemical and physical conditions of the water and causes an increase in nutrients and silicate material. In this poster we present how the tephra deposition can influence diatom assemblage.

Cruces, F., Urrutia, R., Parra, O., Araneda, A., Treutler, H., Bertrand, S., Fagel, N., Torres, L., Barra, R. & Chirinos, L. (2006): Changes in diatom assemblages in an Andean lake in response to a recent volcanic event. Archiv fur Hydrobiologie, 165, 23-35.

Telford, R.J., Barker, P., Metcalfe, S. & Newton, A. (2004): Lacustrine responses to tephra deposition: Examples from Mexico. Quaternary Science Reviews, 23, 2337-2353.

Urrutia, R., Araneda, A., Cruces, F., Torres, L., Chirinos, L., Treutler, H.C., Fagel, N., Bertrand, S., Alvial, I., Barra, R. & Chapron, E. (2007): Changes in diatom, pollen, and chironomid assemblages in response to a recent volcanic event in Lake Galletue' (Chilean Andes). Limnologica, 37, 49-62.

# Session S3 Marine geohazards on the continental margins of Italy: the Magic Atlas

CONVENERS AND CHAIRPERSONS Pietro P.C. Aucelli (Università di Napoli Parthenope) Francesca Boudillon (IAMC-CNR, Napoli) Silvia Ceramicola (OGS, Trieste) Francesco Latino Chiocci (Sapienza, Università di Roma) Fabiano Gamberi (ISMAR-CNR Bologna)

## Coastal response to sea level change in the Garigliano Plain at the Latium-Campania border during the Late Pleistocene - Holocene: constraints for risk assessment

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Keywords: Garigliano coastal plain, borehole data, sea-level change.

We realized a couple of boreholes, both about 16 m-deep, in the Garigliano Plain, a large coastal-alluvial plain located at the boundary between southern Latium and northern Campania. Here we present the preliminary data from the log related to the northernmost drill (CL1). This revealed helpful information about climatic variations and sea level changes. From the bottom, the log is constituted of: i) marine sand with an interbedded primary volcanic layer made of white pumice, half meter thick, ii) silty sand and coarsening-upward yellowish marine sand with, at the top, a reddish horizon of weathered sand, iv) pyroclastic rocks related to the formation of Campania Ignimbrite, v) silty clay and clay of lagoon-marshy environment. From this log, 5 samples have been destined to tephrostratigraphic analysis, 3 to radiometric analysis for age determinations, 48 samples have been collected for paleoecological analysis and about 30 samples for palinological analysis. A similar amount of samples will be tested for mineralogical and geochemical analyses.

Four of the first five samples here examined, coming from the lower part of CL1 drill core, yielded calcareous and siliceous meiofaunal fossil remains. The sample CL1M5 is barren. Foraminifer and ostracod assemblages indicate a shallow marine paleoenvironment characterized by high relative abundances of the foraminifer genus Ammonia and the ostracod species *Pontocythere turbida* and *Semicytherura incongruens*. The absence of miliolid taxa suggests low pH bottom waters, under the influence of volcanic activities.

Preliminary pollen analysis of the lagoon and marsh intervals (CL1 core) indicates the occurrence of a forested landscape dominated by oaks all along the investigated period. Few signs of anthropogenic impact (mainly fires) are evident in the pollen spectra maybe due to the high density of the forest canopy. The presence of dinoflagellates in the basal sample confirms the occurrence of a lagoon environment which is replaced by a marsh, as attested by the increase in *Cyperaceae*.

Thepra analysis revealed the presence of a 39 ky B.P.-old pyroclastic unit, therefore assigned to the Campania Ignimbrite, at about -9 m b.s.l. (bottom) up to -4.50 m b.s.l. (top). This unit presents characteristics indicating that its base represents the first emplaced pyroclastic products of the Campania Ignimbrite. Finally, we can affirm that the basal white pumice layer is not reworked.

In the upper part of the drill core we have recognized lagoonal-swamp facies. On the basis of <sup>14</sup>C dating, we can attribute the starting stage of such a sedimentation to the effects induced by the Post-glacial sea-level rise at about 8000 y BP. The further elaboration of such data can help us to better define the evolutionary frame of the plain in term of sea-level changes and related paleoenvironmental modifications, so permitting us to delineate also the future scenarios of coastal inundation risk.

### A new Megaslide in the Bradano Foredeep area (Southern Apennines, Ionian Sea)

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Keywords: Ionian Sea, Southern Apennines, Foredeep basin.

Along convergent margins, mass-transport represents an important mechanism for sediment distribution within sedimentary basins and, especially if related to seismic activity, it can generate tsunamis. This is also the case of the Gulf of Taranto where mass movements of different size and age are already known. However, a detailed quantitative analysis of geometry, origin, triggering mechanism and final age of their emplacement has not been fully accomplished.

In this study, the submerged portion of the Southern Apennine collisional belt within the Bradano foredeep is investigated. A composite data-set including seismic reflection profiles, exploration wells and seafloor morphology, allowed definition of new large-size Mass Transport Deposit, named the "Bradano Basento Mega Slide" (BBMS) and containing a younger slide mass (BBMS1). The BBMS forms a lens 31 by 19.5 km wide, corresponding to an area of ~396 km<sup>2</sup> A rough depth-conversion allow to estimate a maximum thickness of about ~600 m and a volume of ~130 km<sup>3</sup>. The run-out distance is estimated up to few hundreds of meters. These estimates are conservative, since BBMS and BBMS1 likely have an onshore extension, not imaged by our marine data. This is the largest MTD complex described in the Gulf of Taranto. The BBMS and BBMS1 remobilized toward the SE Middle-Late Pleistocene-Holocene clay/silty-clay deposits. Based on stratigraphic correlations, carried out using well-logs and the ages of correlative deposits onshore, it was emplaced in Late Pleistocene and predated the LGM.

Several lines of evidence, including the fact that the BBMS gliding surface appears to have been controlled by main tectonic structures in the area, suggest that the most likely trigger mechanism for the emplacement of the MTDs is seismic shaking. Thus, it is suggested that BBMS and BBMS1 should be considered paleo-seismological markers of large magnitude earthquakes in the Bradano Foredeep basin. The discovery of BBMS and BBMS1 might be useful to complete the onshore paleo-seismological record and may contribute to clarify the paleo-seismological behavior of this geologically complex area.

The discovery of this new megaslide suggests the need for a re-evaluation of the potential for large earthquakes and tsunamis and in general for a reliable geological hazard assessment along the coast of the Gulf of Taranto, a heavily populated area, site of many industrial infrastructures.

### Plio-Quaternary mass wasting processes along the Ionian Calabrian margin

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Keywords: Mass wasting processes, Ionian Callabrian margin.

The Ionian Calabrian margin is a tectonically active area, and is part of the Calabrian Arc, that is the SE tip of the arcuate Appeninc-Maghrebide fold and thrust belt, generated through the Neogene northwest-oriented subduction of the Nubia plate below the Eurasian plate.

Based on seabed mapping carried out during the national Project MaGIC (Marine Geohazards Along the Italian Coasts), evidences of mass wasting geomorphic features have been identified along the inner continental slope, i.e. slide scars, canyon headscarps and gravity flow deposits.

Two new high-resolution geophysical surveys were recently acquired that extended and improved the existing geophysical dataset: in 2014 the German RV Meteor acquired multibeam bathymetry (50m DTM) and Parasound sub-bottom profiles on a wider area, and in 2015 the Italian RV OGS Explora acquired Chirp sub-bottom profiles and multichannel seismic reflection profiles within the framework of the RITMARE project.

Here we integrate these new data with existing geophysical datasets and published exploration wells to map and characterize submarine slope failures and mass wasting deposits within the Pliocene-Quaternary succession.

The results show mass failures are widespread along the steep (higher than  $10^{\circ}$ ) slopes of the Ionian margin south of Calabria, and within small basins in the inner sector of the calabrian accretionary wedge. Seafloor features range from small-scale features (hundreds of meters in extent), that are mainly located on the canyon headwalls and sidewalls, to larger slides (up to 10 km in extent) on open slopes areas. Subsurface profiles across open slopes and in the small basins provide evidence of repeated failures, in particular in the shallower part of the sedimentary sequence (first hundred meters). The stratigraphic distribution of the mass transport deposits along the Ionian Calabrian margin suggests that the vast majority of the mass transport deposits idenfitied, are observed to occur above an unconformity, which has been tentatively dated to the Middle Pleistocene (<1 Ma). This unconformity seems also to represents the lower bound for the onset of canyon formation. We infer that the onset of both mass wasting and canyon formation could be related to the rapid km-scale differential uplift of Calabria over last 1 Ma, which has driven a seaward tilting of the Ionian Calabrian margin thus leading to mass wasting processes and canyon incision.

# Marine geohazards on the eastern part of Lipari Island (Aeolian Islands): the role of retrogressive erosion at the head of submarine canyons

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Keywords: canyon head, landslide, subsidence.

Lipari is an active insular volcano located in the Southern Tyrrhenian Sea. The recent collection of very high-resolution multibeam bathymetry from the coast down to base of the volcanic edifice allows us to observe a strong asymmetry of its flanks (Bosman et al., 2015; Casalbore et al., 2016). The western side is characterized by the development of large insular shelf related to wave erosion during past sea level fluctuations and is punctuated by eccentric volcanic cones at greater depths. The eastern side shows instead steep flanks affected by several canyons, whose headwall cut back up to 5 meters water depth, few tens of meters far from the coast (Casalbore et al., 2017). These canyons control the shape of the coastline, indicating a strong feedback between the morphogenesis of submarine and coastal sectors. Furthermore, anthropogenic processes overlap on natural coastal dynamics in reducing the sediment input to the eastern Lipari coast. Based on GPS data collected in the last decade and the finding of presently submerged archeological remains (i.e., a roman harbor) at about 12 m water depth, Anzidei et al. (2015) have estimated for the eastern part of Lipari a subsidence rate of 6 mm per year if averaged at the last two millennia and up to 10 mm per year in the last centuries, with significant implication for the flooding of coastal areas. Land subsidence has been mostly interpreted as the result of volcano-tectonic processes, even if the retrogressive activity of canyon head might have played an additional role. In this work, we present a comprehensive view of the potential coastal hazard related to the retrogressive erosion of these canyons, located off the most anthrophized and touristically exploited part of the island.

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# Marine Geohazard associated to the fast-morphological evolution of geologically-active areas: examples from the Southern Italy

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Keywords: retrogressive erosion, canyon head, submarine landslide.

In the last few decades, seafloor mapping (multibeam bathymetry in primis) is drastically changing our vision about the extension and frequency of recent/active geological processes acting in the marine realm, with particular reference to mass-wasting processes. These latter are commonly ubiquitous in all the marine environments, even if they are mostly concentrated in geologically-active areas due to the concurrent presence of several predisposing and triggering factors, such as high sedimentation rates, steep slopes, active tectonics and/or volcanism, etc. Offshore the southern Italy, mass-wasting features were recognized from the coast down to 2600 water depths, affecting from the 52% up to 97% of the whole continental margin (Chiocci and Casalbore, 2017). Furthermore, in these areas mass-wasting processes often occur close to the coast due to the narrow or totally lacking shelves, thus playing a key role in the morphogenesis of coastal sectors as witnessed by the matching of such mass-wasting features with embayment of the coast. In this work, we show different case-studies from the continental margins and submarine flanks of insular volcanoes off Southern Italy, trying to evidence the associated marine geohazard, i.e. their capacity/potential to directly impact coastal and offshore infrastructure or indirectly through the generation of tsunami waves.

Casalbore, D., Chiocci, F.L. (2017): Unexpected fast rate of morphological evolution of geologically-active continental margins during Quaternary: Examples from selected areas in the Italian seas. Marine and Petroleum Geology, 82, 154-162.

### Sedimentary processes and associated geo-hazards of the Ionian Calabrian inner margin

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Keywords: geo-hazard, sediment, Ionian Calabrian margin.

The Ionian Calabrian margin is a tectonically active and very fast morpho-dynamic area where the correlation between the seismic-tectonic activity, widespread gravitational phenomena and the strong dynamism of the mainly structural canyon can be studied. This area provides an opportunity to study active submarine sedimentary processes. The link between these processes and the effects in terms of geological and environmental impact was the focus of a research project entitled *Morphology and Evolution of the Submarine Canyons in the Ionian Margin of Calabria*, led in 2005 by researchers from the Dipartimento di Matematica e Geoscienze of Trieste.

The focus area was the Golfo di Squillace (Calabria) and the aim of the project was to identify and study the connections between seismic-tectonics, the development of submarine canyons and the associated sedimentary dynamics. The first set of geophysical data was acquired during the 2005 cruise (Morelli et al., 2011). A second set of data was later acquired (Ceramicola et al., 2013) within the framework of the MaGIC Project (Marine Geo-hazards along the Italian Coast). During the 2005 oceanographic cruise, the location of 14 sampling stations were chosen on the basis of seafloor morphology. Grabs and gravity cores were collected on the levees and the axes of canyons. Cores are of variable length, between 162 and 282 cm. The samples were recovered at depths between 180 and 1500 meters. A multidisciplinary study has been planned on sediment samples. Continuous measurements (X-rays, Magnetic Susceptibility, XRF core scanner) and analyses on discrete samples (grain-size, mineralogy, organic matter and carbonate content, foraminifera assemblage) are in progress. A significant number of primary tephra layers has been recognized and is being characterized. Several gravitational events are recorded in the sediment. Some of these events could be connected to seismic activity and/or tsunamis as seen in deeper sediment in this and neighboring areas (Polonia et al., 2016). The first data will be presented.

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Morelli, D., Cuppari, A., Colizza, E. & Fanucci, F. (2011): Geomorphic setting and geohazard-related features along the Ionian Calabrian margin between Capo Spartivento and Capo Rizzuto (Italy). Mar. Geophys.Res., DOI 10.1007/ s11001-011-9130-4.

Polonia, A., Nelson, C.H., Romano, S., Vaiani, S.C., Colizza, E., Gasparotto, G. & Gasperini, L. (2016): A depositional model for seismo-turbidites in confined basins based on Ionian Sea deposits. Mar. Geol., DOI 10.1016/j.margeo.2016.05.010.

## Future scenarios of coastal risk due to Relative Sea Level Rise along the Campanian plains (southern Italy)

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Keywords: Coastal subsidence, Marine coastal flooding, Coastal risk mapping.

In Campania region coastal sectors, there are several areas considered to be particularly prone to inundation hazards due to their geomorphological and stratigraphical features, characterized by low topography and relevant subsidence rates. These coastal areas can be affected by the negative impacts of the ongoing eustatic sea level rise, in terms of both erosion and flooding processes, where it is enhanced by local subsidence trends.

In this study we provide an evaluation of the current subsidence rates, derived by the results of the analysis of DInSAR datasets acquired over the Campania coastal sectors from June 1992 to July 2010. New insights into the spatial variability of vertical ground deformations (subsidence/uplift) and their influence on the future marine flooding related to Relative Sea Level Rise (RSLR) along the Volturno, Sarno, Sele and Alento alluvial coastal plains are also provided.

In order to assess the potential coastal flooding hazards, we assumed that the current measured subsidence trend will be kept constant for the near future. The Vertical Ground Deformation (VGD) values obtained by the DInSAR analysis have been used to obtain the future topographic information of the investigated coastal plains, starting from digital elevation model defined by using Lidar data (1 - 2 m cell resolution, 2010-2014 surveys).

The rate of VGD in each cell of DInSAR grid was used to obtain 2065 and 2100 future DEMs by adding the expected change in topography (calculated by using the current deformation rates obtained by DInSAR processing) to the present-day DEM.

The flooding maps for the different sea level rise scenarios derived by IPCC (2014) have been obtained for the studied coastal plains. The inland limit for the flooding analysis has been set at an elevation of 5 m above sea level, including in this way the most susceptible coastal areas.

The areas characterized by susceptibility index and socio-economic exposure index have been combined to identify the hotspot areas with the highest potential coastal risk. The indices have been evaluated for coastal sectors 1 km wide, according to the CRAF methodology (phase 1) of the RISC-KIT index-method, based on indicators referring to land use categories, economic activities and social vulnerability.

The results about Campania potential coastal flooding risks exhibit a different distribution into the plains, due to the differential rate of the estimated subsidence referred to the 2065 and 2100 IPCC scenarios. The obtained results highlight with a high resolution the importance of the DInSAR data for the spatial susceptibility assessment to the coastal areas flooding. RSLR scenarios suggest that in the near future natural areas, beaches, human infrastructures, and wide portions of agricultural areas located in the plain will be affected by potential marine flooding, with several zones falling within high risk areas.

IPPC (2014): Intergovernmental Panel on Climate Change - Fifth assessment report. Climate change 2014. Cambridge University Press, Cambridge.

# Geomorphic setting and sedimentary processes in the North-Eastern sicilian continental shelf: hints for offshore geohazard evaluation

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Keywords: highstand wedge, delta systems, canyon head.

The northeastern Sicilian continental shelf, between Capo Milazzo and Capo Rasocolmo, extends for about 25 km in SSW-NNE direction, with average width of about 3.5 km. It is located along a tectonically active margin, with large rate of differential vertical movements linked to the structural framework of northeastern Sicily and southern Calabria. Continental shelves are the submarine areas closest to land and riverine sediment transport, albeit in combination with oceanographic processes, is the main control for their geomorphic setting. In addition, climate and tectonics operate at different spatial and temporal scales in controlling the character and the site of sediment accumulation. The aim of this work is to provide, through Multibeam bathymetric data, an update characterization of the geomorphology and sedimentology of the northeastern Sicilian continental shelf. Furthermore, the morpho-stratrigraphic description of the transgressive and highstand wedges is carried out through high-resolution CHIRP seismic profiles, and a reconstruction of the deposits of the last eustatic sea level cycle is provided. A considerable part of the external, relict shelf, between Rometta and Villafranca canyons, is characterized by sedimentary bodies, with an highly reflective acoustic facies, that have been interpreted as a transgressive wedge, that often clearly show the character of past coastal landscapes. It lies in unconformity on a continuous erosional surface, which is interpreted as the top of the lowstand wedge. In the western and central portion of the study area, several relatively large rivers provide a considerable sedimentary input and form deltas. Delta building in the coastal area is associated with distributary channels that continue further offshore. The development of delta deposits is a function of space availability for their progradation in the continental shelf. In fact, where the shelf is very narrow and the head of the canyons is close to the shoreline, the delta distributary systems show a rather narrow expansion and the rivers discharge their sedimentary load into the canyons. Conversely, where the accommodation space is greater, the distributary channels occupy a wider shelf portion and distal prodelta deposits reach the shelf edge. In the eastern portion of the shelf, the low sedimentary contribution from small rivers results in a limited expansion of the highstand wedge that is restricted to the inner sectors of the shelf. Here, the influence of the oceanographic currents driven by the Strait of Messina is crucial in the formation of sediment wave fields and possibly of an infralittoral prograding wedge. Our analysis shows that elements of hazards in the shelf have variable origin and can affect either directly the coast, such as the coastal connected canyon heads, or more in general the entire width of the shelf where a vigorous sediment dynamics result in an mobile seafloor that can pose a threat to offshore infrastructures.

# Extensive mass-transport deposition in the Capo d'Orlando Basin: location, 3-D geometry, facies and possible genetic processes

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Keywords: debris-flow deposit, channel-levee wedge, shelf-edge.

Downslope sedimentary processes, driven by gravitational forces, move material over the seafloor and resediment it into deeper water. These processes are characterised by a large variety of magnitude, types of transport and deposition, and frequency. Resulting mass transport deposits (MTDs) are found on the slope, at the base of slope and on the basin floor. MTDs can represent a large portion of the stratigraphic infill of some basins around the world. This is the case of the recent sedimentary succession of the Capo d'Orlando Basin, where a remarkable variety of MTDs is present and is illustrated in this work. Our analysis focusses on: the location of the evacuation and depositional areas of the MTDs; the characterisation of the surface geomorphology of the MTDs, both in their evacuation and accumulation areas; the evaluation of the thickness and 3-D geometry of the MTDs; the determination of the MTDs' facies. The MTDs' evacuation areas are mainly restricted to the slope, but some of them propagate upslope to affect the shelf-edge. The largest MTD occupies the entire eastern part of the basin plain with a total volume of approximately 12 Km<sup>3</sup>. It is a frontally unconfined slump often having an erosional base and a ramp geometry in its frontal area. Intermediate-sized MTDs form an apron at the base of slope and do not reach the basin plain. Their evacuation areas are in the channel-levee wedges that consequently are experiencing a major destructional phase. Smaller scale MTDs are present in the upper slope; they are debris flow deposits generally having an axial channel and lateral and distal blocky "wings". Larger MTDs are however also present in the upper slope of the western basin portion; they have a blocky surface and their evacuation area involves the shelf edge and is probably controlled by tectonic structures. The shelf edge is affected by sediment failure also in the eastern part of the basin. Here, landslide results in the retrogradation of canyon heads that reach the coast. They can be triggered by rapid events of high sedimentation at the shelf edge, possibly connected with hyperpycnal river discharge or oceanographic processes, and lead to flows that flush the canyons. The basin-plain MTD and the base-of-slope MTDs can result from a single failure event or from almost synchronous multiple events indicating a major pulse of widespread instability in the basin margin. Mass-transport deposits can occur at any time during a margin's history but commonly they form thick accumulation due to accentuated seafloor instability, often associated with specific periods during a cycle of sea-level variations. Also the common occurrence of MTDs in the stratigraphy of the Capo d'Orlando Basin points to a recent intensification of sediment collapse. However, in this case, widespread mass-wasting processes have their roots in the tectonic setting of the northern Sicilian margin with active faulting, tilting, vertical movements and seismicity.

# Holocene coastal geomorphological evolution in response to sea level rise: a validation for future scenarios of marine flooding along the Campanian coastal plains

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Keywords: Relative sea level change, Marine coastal flooding, Campanian coastal plains.

In this work, Holocene geomorphological coastal evolution in response to sea level rise has been compared to future sea level rise projections evaluated for some Campanian coastal plains (Volturno, Sele and Alento plains). In this way, the flooding scenarios estimated for the end of 21<sup>th</sup> century (Lambeck et al. 2011; Aucelli et al., 2017; Di Paola et al., 2017, Matano et al., 2018) can be validated.

The Holocene evolution of these areas has been mainly controlled by a marine transgression due to postglacial sea level rise, which caused the formation of sandy barriers and lagoonal systems that fast migrated landward. At the end of this transgressive phase, the shorelines prograded several hundred meters mainly for the decrease of the sea level rise rate.

To date, the Campanian alluvial coastal plains host several low-land areas usually localized at the back of the sandy coastal dunal ridges and around the river mouths. These areas results particularly prone to be affected by the negative impacts of the sea level rise, also enhanced by local subsidence.

The comparison between the future relative sea level rates and sea level rates since 10.000 years BP has been carried out by plotting the predicted local sea level rise rates in a graph where Holocene coastal geomorphological trends are represented. Three fields of coastal response have been defined: a) flooding and prevailing coastal retreat phase; b) transitional phase; c) prevailing coastal progradation phase.

The local sea level rise has been evaluated as sum of the eustatic component and the ongoing ground deformation trends, estimated by DIn-SAR data.

The results enhance that the studied coastal plains fall in the flooding field of the proposed diagram when subsidence rates are coupled with predicted sea level rise rates. Furthermore, the comparative analysis leaves no dubs that no one of the future estimated local sea level rise trends can be compensated by progradational pulses of the plains.

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Lambeck, K., Antonioli, F., Anzidei, M., Ferranti, L., Leoni, G., Scicchitano, G. & Silenzi, S. (2011): Sea level change along the Italian coast during the Holocene and projections for the future. Quaternary International, 232, 250-257.

Matano, F., Sacchi, M., Vigliotti, M. & Ruberti, D. (2018): Subsidence Trends of Volturno River Coastal Plain (Northern Campania, Southern Italy) Inferred by SAR Interferometry Data. Geosciences, 8(1), 8.

# Geological evolution and land subsidence of the Volturno River coastal plain (northern Campania)

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Keywords: Volturno alluvial plain, Holocene incised valley fill, Geotechnical properties.

Most of the world's floodplains are affected by subsidence, a phenomenon that includes, among others, the salinization of the aquifer, coastal erosion, greater vulnerability to flooding and storm surges, structural damage to infrastructure. In the Mediterranean, numerous floodplain plains are affected by subsidence due to both the rise in global sea level and other natural and anthropogenic factors. In analyzing the potential drivers of subsidence, in recent times the sedimentological evolution of modern river deltas has been considered, which began to form around 6500 years, after the fall of sea level in the last glacial phase (Last Glacial Maximum - LGM) and the subsequent aggradation and Holocene progradation. The Incised Valleys (IV) formed during the LGM were filled by fluvial-lacustrine, transitional and marine deposits, characterized by sands, silts, clays and peat. Recent studies confirm that natural compaction can cause a decrease of several millimeters for years, especially in coastal deposits rich in organic substances.

The aim of the present study is to define the stratigraphic architecture of the Holocene and the correlation with the ground deformation trends referring to two decades (1992-2010), which characterize the coastal alluvial plain of the Volturno River, in northern Campania. Assessment of subsidence trends was previously based on SAR (Synthetic Aperture Radar) interferometry techniques.

The reconstruction of the satellite time series shows a general tendency to the ground subsidence over time of the whole area and a strong negative subsidence in three sites between the coast and the lower valley of the Volturno. The reconstructed stratigraphic architecture has shown that the unit which is the first substrate for Holocene and Recent sedimentation is represented by the Campania Grey Tuff (CGT), produced by the explosive volcanic activity of the Phlegrean Field about 39 ky and deposited over the whole Campana Plain. The CGT was deeply eroded by the fluvial activity during the LGM and the resulting Incised Valley was subsequently filled by fluvial-lacustrine, transitional and coastal deposits.

The spatial intersection of the deformation data with the geological data showed a net overlap of the subsiding areas with the paleovalley contour. Furthermore, higher subsidence rates affect areas characterized by thicker Holocene sedimentary sequences and in particular where silt, clayey silt, clay and peat are the main lithologies. The latter, from a geotechnical point of view, are classified as fine grained soils with poor mechanical properties (high compressibility and low resistance). Furthermore, the inclusion of a significant amount of peat and organic matter is reflected in high values of secondary consolidation coefficient.

This suggests that if anthropic activities can be the cause of a generalized process of primary consolidation, a key role is played by sthe tratigraphic structure and in particular by distribution and thickness of Holocene deposits, whose characteristics are at the origin of secondary consolidation and of the variability observed among subsidence rates.

The results of this study confirm the importance of an integrated study for the assessment of hazards to coastal areas.

# Open-slope, translational submarine landslide in a tectonically active continental margin: the Licosa submarine landslide (South-eastern Tyrrhenian Sea)

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Keywords: underwater sediment failure, Y-5, weak layer.

The southern Campania continental margin seems prone to failures along stratigraphic weak layers. At least eight translational landslide systems (single or complex) larger than 20 km<sup>2</sup> have been identified in the bathymetric range 200-700 m, over about 1000 km<sup>2</sup>. An area of about 30 km<sup>2</sup> of the upper slope in water depths of 200 -300 m, off Licosa Promonty (South-eastern Tyrrhenian Sea), failed between 14 ka and 11 ka BP. We approached the study of the Licosa landslide by multibeam- and CHIRP- sonar surveying, high-resolution multichannel seismic profiling and coring, to assess the morphology, the stratigraphy and the structural discontinuities in the area (Sammartini et al., 2018 and references therein). Specifically, samples include some fall-controlled piston cores retrieved in-scar and out-of-scar, aimed at investigating the mechanical properties of the failed soils. This analysis revealed that the landslide detached along the outer, gentle (dipping about 1.5°) slope of the last glacial shelf wedge and involved at the base the fall-out pumice lapilli deposit of the Y-5 (39 ka) volcanic event. The settlement of the tephra gave rise to a distinguishable seismic marker over a great extent of the southern Campania offshore. Several previously unknown geological features of the continental margin are likely to have favored the slope instability in the area. These are the basal erosion of the slope in the Licosa Channel, the high sedimentation rate in the sedimentary wedge, the litho-stratigraphic discontinuities, the gas/fluid migration zones occurring in the surrounding 15 km, and possibly the lateral pore water flow from the depocentre of the wedge to the base of the slope, along the high-permeable layers. However, further investigations are needed to develop a coherent chronological framework among the processes. A prominent structural discontinuity, E-W oriented, and several associated normal faults displaced the acoustic substrata and the sedimentary succession up to the late Middle Pleistocene. This lineament has been here acknowledged as possibly being the fault whose activity may have triggered the slope instability in the area, trough earthquake shaking. The time span activity and geometry of the fault well match the structural framework of the last deformation event, currently active inland, and set in the geodynamical context of the Pleistocene-Recent back-arc extension of the Marsili basin.

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Sammartini, M., Camerlenghi, A., Budillon, F., Insinga, D.D., Zgur, F., Conforti, A., Iorio, M., Romeo, R. & Tonielli, R. (2018): Open slope, translational submarine landslide in a tectonically active volcanic continental margin (Licosa submarine landslide, Southern Tyrrhenian Sea)" In Lintern, D. G., et al., Eds., Subaqueous Mass Movements. Geological Society, London, Special Publications, 477, <u>https://doi.org/10.1144/SP477.34</u>.

### Nature and origin of fault-controlled fluid seepage across the Maltese Islands

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Keywords: pockmark, fluid flow, flares.

The Maltese Islands are intersected by two major fault systems associated with two diverse rifting episodes affect the islands. The first and most widespread system is Early Miocene to mid-Pliocene in age, and consists of faults that are orientated ENE-WSW. The most distinct of these faults is the Great Fault (known also as the Victoria Lines Fault). The younger system of faults (Late Miocene-Early Pliocene) is still active and consists of faults striking NW to SE that often cross-cut the first generation of faults. The most extensive of these faults is the Maghlaq Fault, located along the southern coastline of the Maltese Islands.

The objectives of this study are to characterise active fluid flow systems across the Maltese islands, identify their origin and infer the mechanisms by which fluid is transferred to the seafloor. To fulfil these objective we merge seismic reflection profiles (boomer, multichannel and sub-bottom), high-resolution multibeam echousounder and CTD data, water and seabed samples, stratigraphic logs (that were calibrated with the seismic lines), aerial data (to determine methane and carbon dioxide concentrations in the atmosphere) and terrestrial data (i.e. water geochemistry interpretation, dissolved gas geochemistry and soil gas measurements).

Fifty-eight pockmarks with sub-circular planform shapes and U/V-shaped cross-sections have been. Their mean axis is about 12 m in diameter and the wall slope gradient is 3-4°, while their mean depth is 4 m (over the range 3-15 m). In the water column, gas flares attributed to the occurrence fluid escape and showing anomalous amplitude peaks have been mapped at the top of the pockmarks. A number of gas chimneys extending up to seafloor have been identified using the boomer and the multichannel seismic lines in the sub-seafloor. The CTD data showed some local anomalies where a major decrease in conductivity is observed without a larger change in depth. The geochemical analysis of the water samples collected at the top of the pockmarks showed for the first time in this area data on the presence of  $CH_4$ ,  $CO_2$ , He and other gases dissolved in the bottom seawater. Dissolved gas and soil gas measurements allows us to recognize the presence of atmospheric (N<sub>2</sub> and O<sub>2</sub>) and non-atmospheric gas species (such as  $CO_2$ ,  $CH_4$  and He).

We identify two main fluid flow systems. The first consists of a shallow system where fresh-water actively seeps at the seafloor, likely through a connection with terrestrial aquifers. The second type comprises deep fluids that ascend through the Early Miocene to recent faults and gas chimneys, forming pockmarks at the seafloor. Considering the good correlation between tectonic structures and gas-seepage signatures (pockmarks, gas chimneys and gas flares), we suggest that fluid migration and expulsion are at least driven by extensional and transtensive tectonic structures affecting the Maltese Islands.

# A multidisciplinary study of a sinkhole along the southern metamorphic coast of Paros island (Greece)

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Keywords: Geoswim, coastal geomorphology, coastal karst.

In spring 2017 we explored Paros, in the Cycladic islands (Greece). During the survey, we carried out an integrated study of a sinkhole, from the seaside, using the Geoswim approach, and on-land, through field and drone surveys. The Geoswim project was introduced in 2012 to combine snorkel and field surveys and to analyze in detail the coastal landforms, their lateral variations and to acquire information about past and future sea-level changes.

This site is located along the southern coast of Paros. The sinkhole develops as a roof-collapsed oval-shaped cave, opened to the sea.. The bedrock is composed by layered Mesozoic marble of the blue-schist facies of the lower unit of the Attic-Cycladic complex and minor non-carbonate lithotypes. The site is affected by folding and faulting responsible of intense deformation and fracturing of the affected lithologies.

The sinkhole is 10 m high, 41 m long and 2 m large Its bottom is partially covered by blocks collapsed from the lateral cliffs. Its maximum depth is about 8 m at the entrance

Drone surveys have been realized to reconstruct a high resolution Digital Terrain Model both of the sinkhole and the surrounding coastal area. Two flights at elevation between 30 m and 40 m have been performed. Data were elaborated to product a DTM (2x2) cm resolution and an Ortophoto 3cm/pixel of resolution. Both let to detect and survey, with high accuracy and precision, several important morphological futures such as fractures, detached or fallen blocks.

Physical/chemical data allowed to locate small submarine springs whose activity are probably related to high rainfall periods.

Time-lapse images collected at the sea level allowed to describe in detail the micromorphology and biological zonation of the tidal zone, at the entrance and inside the sinkhole. The entrance is dominated by sub-rounded surfaces from the bottom to the roof. Millimetric to decametric rounded-shaped holes show a biological activity at the tide level.

We observed a distinct biological zonation outside and inside the sinkhole. The open coast shows the current zonation of most Mediterranean coasts, with *Patella rustica, Patella caerulea, Chthamalus, Titanoderma trochanter* and *Phorcus mutabils*.

We hypothesized that tectonics and erosive processes determined the formation of a former sea cave and subsequently, after the collapse of the roof, the sinkhole, or roof-less cave. Joints weakened the bedrock down to the production of small blocks, and the wave action promoted not only the partial collapse of the roof and the cliff, but also the seawards removal of resulting blocks and, above all, of the high-erodible non-carbonate rocks. These processes sub-excavated the bedrock until the roof collapsed, resulting in the formation of the sinkhole. These kind of karst processes produce significant hazard for coastal activities.

# **Session S4**

The role of Italian scientists and educators in the International Ocean and Continental Drilling Programs: major achievements and new perspective

> Conveners AND CHAIRPERSONS Claudia Lupi (Università di Pavia) Annalisa Iadanza (IAMC-CNR) Marco Sacchi (IAMC-CNR) Fabio Florindo (INGV-Roma) Patrizia Ferretti (Università di Venezia)

# **IODP EXPEDITION 357: Atlantis Massif Serpentinization and Life**

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Keywords: Atlantis Massif, serpentinites, IODP 357.

Expedition 357 "Atlantis Massif Serpentinization and Life" was the first Mission Specific Platform (MSP) expedition implemented by the ECORD Science Operator (ESO) in the current phase of the International Ocean Discovery Program (IODP; Früh-Green et al., 2016). An east-west transect across the southern wall of the Atlantis Massif was cored to study the links between serpentinization processes and microbial activity in the shallow subsurface of highly altered ultramafic and mafic sequences that have been uplifted to the seafloor along a major detachment fault zone. Seventeen holes were drilled at nine sites across the Atlantis Massif, recovering more than 57 m of core, with borehole penetration ranging from 1.3 to 16.4 meters below seafloor and core recoveries as high as 75% of total penetration. The cores show a highly heterogeneous lateral and vertical distribution of ultramafic, mafic, and sedimentary rocks with a wide range of alteration styles and extensive alteration and deformation. Of the core recovered from six sites across the southern wall (from west to east: M0071, M0072, M0069, M0076, M0068, M0075), serpentinized ultramafic rocks are predominant (44% by length of core). Other major rock types include basaltic rocks and metadolerites (combined 24%) and schistose metasomatic rocks with varying proportions of talc, amphibole and chlorite (11%). Minor lithologies include calcareous sedimentary units (8%) and gabbroic rocks (4%). The rock types, textural characteristics and proportion of gabbroic rocks recovered during Expedition 357 are distinctly different from the 1400 m-long core of gabbroic rocks recovered during IODP Expedition 304/305 at the central dome of the Atlantis Massif (Blackman et al., 2006). The ultramafic rocks are dominated by harzburgites punctuated by intervals of dunite and minor pyroxenite veins; gabbroic rocks occur locally as zones of melt impregnation and veins, all of which provide information about multiple magmatic processes and evolution in the southernmost portion of the Atlantis Massif. On-going geochemical studies aim to provide a detailed description of these drilled rock sequences in order to estimate the conditions of alteration and their scales of heterogeneity during the detachment faulting at the slow-spreading ridges.

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## Uncovering the Mediterranean salt giant

# Camerlenghi A.\*<sup>1</sup>, Lofi J.<sup>2</sup>, Bertoni C.<sup>3</sup>, Aloisi G.<sup>4</sup> & all the co-proponents of the MEDSALT, DREAM and SALTGIANT initiatives

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Keywords: Messinian Salinity Crisis, Scientific drilling, Mediterranean.

About 6 million years ago the Mediterranean Sea became an enormous saline basin where more than one million cubic kilometres of salt accumulated, locally exceeding a thickness of 3 km in the deep basins. This extreme, but geologically brief event (640 ka; the so-called Messinian salinity crisis MSC), changed the chemistry of the global ocean and had a permanent impact on both the terrestrial and marine ecosystems of a huge area surrounding the Mediterranean. Drilling the MSC salt giant represents a unique opportunity to understand the sedimentary history, stratigraphy, biosphere and fluid dynamics of a salt giant in a state close to its original depositional configuration, and to understand the responsiveness of a land-locked oceanic basin to planetary dynamics.

The multi-phase drilling proposal "Uncovering a Salt Giant" addresses four overarching scientific questions:

- What are the causes, timing and emplacement mechanisms of the MSC salt giant?
- What are the factors responsible for early salt deformation and fluid flow across and out of the halite layer?
- Do salt giants promote the development of a phylogenetically diverse and exceptionally active deep biosphere?
- What are the mechanisms underlying the spectacular vertical motions inside basins and their margins?

It is being implemented through two site-specific riserless drilling pre-proposals:

"Deep-Sea Records of the Messinian Salinity Crisis (DREAM)", targeting a transect of sites on the southern margin of the Balearic promontory. Unlike most of other Mediterranean margins that have undergone MSC erosion, the south Balearic margin has been identified as the only place in the Mediterranean where well-defined and almost un-deformed MSC deposits are found in a series of sedimentary basins lying at different water depths between the present-day coastline and the deep central salt basins.

"The demise of a salt giant: climatic-environmental transitions during the terminal Messinian Salinity Crisis", targeting two pairs of sites in the Ionian Sea and in the Levant Basin. In these deep basins, the record of the last stages of the MSC, including Lago Mare facies and the upper part of the evaporite/clastic series, which were not fully cored in previous scientific drilling campaigns is accessible for understanding of the hydrological connectivity among all sub-basins and with the Paratethys, the response of major circum-Mediterranean rivers to the demise of the Messinian salt giant and the link between evaporite formation, microbial activity and dolomitization.

After the successful submission of the two pre-proposal, the activity is now cantered in the completion of the Site characterization package in view of the submission of the full proposals. Unexpected difficulties with the public acceptance of the geophysical surveys and the future drilling are jeopardizing the success of this scientific effort.

#### "Campi Fegrei Deep Drilling Project": the history of a controversy

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Keywords: Campi Flegrei, communication, citizens.

The aim of the Campi Flegrei Deeep Drilling Project (CFDDP) was to increase the level of knowledge about the Campi Flegrei caldera, by directly investigating the deepest rocks down to a depth of ca 4 km, close to the area of possible magma accumulation that fed the caldera system during the last bradyseism crisis. The first phase of the project, completed in December 2012, saw the drilling of a pilot well, up to 500 m deep, in the eastern sector of the caldera, within a former industrial area, in the plain of Bagnoli (in the municipality of Naples).

Beyond the scientific results that the CFDDP has produced up until now, the experience itself served to touch on the problem of communication between science (and scientists) and citizens. In fact, before the starting of the project the community and the local authorities were worried about the risk related to the drilling. The main concerns were fostered when the debate among scientists (promoters and detractors of the project), about the usefulness of the drilling, became very animated. Among the voiced risks there was one of concerning the eventuality of triggering an eruption just by drilling into the caldera. The entire research team involved in the CFDDP soon realized that they were dealing with something that did not strictly concern the scientific community and its internal dynamics. Rather, it was necessary to show the population exposed to risk how science works, the methods it uses and above all the entity of the real risks in tackling a project of this magnitude. I will try to explain the history of this controversial project and the role that scientists played in the evolution of knowledge of Campi Flegrei caldera that is one of the highest volcanic risk areas in the world.

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Keywords: Research Experiences for Teachers, Education, Outreach.

IODP (International Ocean Discovery Program) and ECORD (European Consortium for Ocean Research Drilling) provide several opportunities for teachers among which the chance to sail onboard a drilling vessel during a research expedition. The role of the teachers on board is to work as *Education and Outreach Officers*. They are responsible for disseminating the results of the research that is carried out on the ship to a wider public as possible, especially to students of every school year.

The involvement of the teachers in a two-month ocean drilling expedition can be considered as a Research Experience for Teachers (RET), a kind of professional development that requires science teachers to be directly involved in research activities while working side by side with scientists with mutual benefits.

In this study, we analyse the outcomes of the seven teachers' experience as *Education and Outreach Officers*. The teachers, who took part in various expeditions, come from five European member Countries of ECORD. The research questions considered in this study are:

1) How effective is the participation in a research Expedition on improving the knowledge of a scientific topic for the teachers involved (in this case the research based on ocean drilling)?

2) What is the effect of these experiences on teachers with regards to the use of inquiry in their classrooms and their teaching approach?

3) How did the participating teachers change their self-perception of their identities in relation to doing Science and being a scientist?

The approach of the study is qualitative and the instruments used are surveys and semi-structured interviews.

Overall, the teachers involved in the program reported that they gained great benefits of the experience on board and that it also represented a professional development for them. The majority of the teachers noted an increase in their scientific knowledge, in self-confidence in teaching using inquiry, a greater awareness of scientific careers (in view of orienting their students) and in doing research. Many of them, in fact, are still collaborating with the scientists they met during the expedition and have participated in conferences and workshops in order to disseminate their experience.

This exploratory study, despite the amount of bias due to the small group of teachers involved, shows that the opportunity to sail on an IODP/ECORD expedition and be immersed in the research process can be considered an effective professional development for science teachers. Furthermore, this kind of experience has led to long-lasting results in terms of their teaching activities and inclination to doing research. The major part of the data we investigate is self-reported, therefore future development of this study could become an experimental study in order to evaluate the effectiveness of the teachers' research experience on their students' achievement in science and the impact on their students' future university choices and careers.

# Miocene oceanographic evolution of the Central Mediterranean: Insights from the Sr and Nd isotope records

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Keywords: Adriatic domain, Central Mediterranean, Miocene.

The Miocene is a key interval in the geodynamic and oceanographic evolution of the Mediterranean basin since it marks the transition from a wide open basin to the modern closed one. In this work, we present the Sr and Nd isotope records of two Miocene carbonate successions in the Adriatic domain to document how the evolution of the Mediterranean basin controlled its seawater chemistry. During the late Aquitanian (21.8 Ma), a sea level low-stand phase related to a glacial maximum led to an increased continental-derived runoff due to an enhanced weathering affecting the 87Sr/86Sr isotope signature of Mediterranean seawater. Whereas, the Burdigalian Mediterranean <sup>87</sup>Sr/<sup>86</sup>Sr ratios are significantly lighter than the coeval global ocean signal, demonstrating that the volcanism in the circum-Mediterranean area mainly influenced its Sr isotopic signature. Lastly, during the late Miocene the Mediterranean sub-basins, e.g. the proto-Adriatic basin, suffered restricted water conditions due to the elongated and shallow physiography of this basin, and accordingly the Sr isotopes fell below the global reference line. In contrast, the long-term Nd isotopes trend approximates the transition from a wide-open basin, mainly influenced by the Indo-Pacific Ocean, to the modern closed basin connected with the Atlantic Ocean only through a narrow strait. In fact, the early Miocene Nd isotope data testify that the major water mass flew from the deep Indian Gateway, and the Indo-Pacific Ocean mainly controlled the Central Mediterranean water body. During the Langhian (15.97-13.82 Ma), a time of sea level high-stand associated with the Middle Miocene Climatic Optimum, the Nd isotope values indicate that waters exchanged between the Paratethys and the Central Mediterranean. The Central Mediterranean was well connected with the Atlantic Ocean between the Langhian and the early Tortonian, while the exchange of water with the Paratethys declined. Lastly, the early Messinian Nd isotope data are coherent with the Sr isotope record, confirming an influence of Atlantic waters partly contaminated by local freshwater input. In this context, increased freshwater input and continental derived runoff, enhanced by the eastward migration of the Apennine accretionary wedge, mainly controlled the proto-Adriatic basin's water chemistry. Lastly, we affirm that the Nd isotope record of Mediterranean waters was never the same as the open ocean signature, but always a mix of two opposite signals: the main circulation patterns and the local geodynamic evolution. However, the comparison of the local Nd isotope signal with the open ocean curves yields the information on which ocean mainly affected Mediterranean waters during the different stages of its evolution.

# Late Cenozoic ocean-ice sheet interactions and West Antarctic Ice Sheet vulnerability: Initial results from International Ocean Discovery Program Expedition 374 in the Ross Sea continental margin

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Keywords: International Ocean Discovery Program, JOIDES Resolution, Expedition 374.

International Ocean Discovery Program Expedition 374 cored five sites in the Ross Sea in January-February 2018. The geological records recovered the distal component of a Neogene latitudinal and depth transect across the continental shelf and rise, that will be combined with previous ANDRILL and Deep Sea Drilling Project (DSDP) Leg 28 records comprising the ice-proximal component. This transect design following the SCAR/PAIS approach will allow us to investigate the role of oceanic drivers of marine ice sheet instabilities. The existing reflection seismic data suggest that intervals with limited ice cover occurred among episodes of grounded ice that extended to the shelf margin during the Neogene. The objectives of Expedition 374 are to 1) Evaluate the contribution of West Antarctica to far-field ice volume and sea level estimates; 2) Reconstruct ice-proximal atmospheric and oceanic forcing (e.g., sea level and temperature) on Antarctic Ice Sheet stability/instability; 4) Identify the sensitivity of the AIS to Earth's orbital configuration under a variety of climate boundary conditions; 5) Reconstruct eastern Ross Sea bathymetry to examine relationships between seafloor geometry, ice sheet stability/instability, and global climate.

Following initial shipboard characterization of the cores during Exp. 374, the correlation between synthetic logs at the new drill sites and the crossing seismic sections will provide crucial information about the age and the environmental conditions during the deposition of glacial and marine strata. Changes in the bathymetry of the continental shelf are important for understanding the dominant West Antarctic Ice Sheet mass balance controls. The stratigraphic information from Exp. 374 will allow us to create well-dated paleobathymetric maps of the main seismic unconformities and therefore provide a measure of the geomorphological changes under the action of the ice sheet and ocean circulation. The results will be fundamental for numerical ice sheet models aimed to infer the past Antarctic volume fluctuation contribution to Neogene sea-level changes.

#### Italy and Ocean Drilling: a 50-year history of dreams, expectations, successes and training

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Keywords: ocean drilling program, IODP-Italy.

This year the scientific community celebrates the fiftieth anniversary of the international project of scientific ocean drilling that is the largest, longest and most innovative research program ever conceived in the field of Earth Sciences. Italy has participated in this project since 1969: it has given and continues to give generations of senior and junior Italian geoscientists the opportunity to gain experience and contribute to the international community of marine geology. The Italian contribution to the DSDP-ODP-IODP project is internationally recognized for the excellent scientific quality of the research carried out before, during and after cruises. Many Italians were on board and/or studied the material recovered at over 1500 sites so far, and signed dozens of drilling proposals as co-proponents. Also, Italian geoscientists help to keep the farsighted, innovative and educational program capable of continuously renewing itself remaining on research frontiers.

Through ocean drilling, we have learned so much about the Earth System, its exogenous and endogenous processes: the systematic exploration and coring of the ocean floor and sub-seafloor, even in extreme areas, has led to the formulation of plate tectonics, to the modeling of short- and long-term climate changes, to discovery of the deep biosphere, to numerical characterization of marine geohazards including earthquakes and tsunamis. But there is still much to do, to explore, and to understand: we must not sit on the laurels of a program of undisputed success: we all must persist learning from achievements and mistakes.

The Italian community, after a period of national funding and coordination has also gone through difficult times that have almost enforced the participation in IODP. But the strength of the ocean-drilling program has managed to support efforts to get to IODP-Italy: we will remain in IODP and continue to be co- protagonists of this exciting program.

#### IODP Exp. 353 "Indian Monsoon Rainfall": what comes after the Cruise...

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Keywords: IODP Exp. 353, diatom biostratigrapher, post-cruis preojects.

IODP Expedition 353 "Indian Monsoon Rainfall" (November 2014 - January 2015) took place in the Bay of Bengala (BoB) on board of the RV JOIDES Resolution. I took part to the Expedition during my second PhD year as a diatom biostratigrapher. The experience on board increased both my skills as micropaleontologist and my scientific network; also it gave me the chance to start three post-cruise projects. The first will take advantage of most of the smearn slides that were prepared on board and aims to compile a new Neogene diatom biostratigraphic scheme for the BoB. Currently biostratigraphic schemes calibrated within the Bay of Bengal are lacking; indeed, scientific drilling programs had never reached north of IODP Site 758 (ca. 9° N) before Exp. 353. This project will be realised thanks to the collaboration with the other micropaleontologists (M. Bartol, C. Bolton, X. Ding, O. Romero, M. Robinson) and paleomagnetists (S. Taylor, Y. Usui) that took part to the cruise. The second project will investigate Miocene samples from Site U1447 (Andaman Sea) to investigate the "Late Miocene carbon isotope shift" (ca. 7.6 - 6.6 Ma), which can already be pinpointed in onboard data on diatom abundance. The project will benefit from the collaboration of Prof. Caterina Morigi (Università di Pisa) and of Prof. Alessandra Negri (Università Politecnica delle Marche), who will integrate the analysis on diatom assemblages with those on fossil nannoplancton and foraminifera. We will discuss and compare our results with other Cruise participants who are investigating the same event by means of other methods or at other Sites. Finally, a third project called "Role of Volcanic Ashes in Enhancing Primary Production: Evidences in the Deep Time" is meant to investigate the fertilization capacity of volcanic ashes as they reach the ocean surface following volcanic explosive events. Thanks to the collaboration with Dr. Anna Gioncada (Università di Pisa), Prof. Caterina Morigi (Università di Pisa) and Prof. Matthias Zabel (MARUM, Brema), this project, which was founded by ECORD (ECORD Research Grant 2015) has already had some interesting results.

# Spotting the evidence of the effect of volcanic ashes on primary production: report on on-going studies from sites U1443, U1445, U1447 and U1448

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Keywords: IODP Exp. 353, volcanic ash, paleoproductivity.

Numerous ash layers were recognised in the sediments collected during IODP Exp. 353, in the Bay of Bengal (BoB). The recovery of these ashes gave us the opportunity to undertake a study on the effects of the deposition of volcanic ash on primary production by analysing the sediment archives. Indeed, this phenomenon has been investigated by numerous previous studies in today oceans, highlighting different responses of the phytoplankton: right after the deposition of volcanic ashes on the sea surface, some authors noticed a decrease in the primary production, while some others observed anomalous algal blooms. To start our research, we selected ash layers from sites U1443, U1445, U1447 and U1448. One tephra layer, supposed to correspond to the younger Toba event, was selected from every site, in order to compare potential ash fertilization mechanisms of the same volcanic event at increasing distances from the volcanic source. Two additional tephra were selected from Site U1443, to verify how much ash fertilization in a given area can be influenced by the geochemical and morphological characteristics of the ashes themselves. Geochemical, petrographic and micropaleontological investigations have been carried out on the bulk sediments. The approach we used is innovative, since we have investigated the trend of paleoproductivity proxies below and above the tephra and compared them to the response of microplanktonic organisms to the deposition of volcanic ash at high resolution (0.5-1 cm). Here we present the results concerning the geochemical investigations and some preliminary petrographic and micropaleontological results.

# The importance of Ocean Drilling Program expeditions for Mediterranean Sea Palaeoenvironmental and Palaeoceanographic research

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Keywords: Ocean Drilling Program, Mediterranean Sea, Paleoceanography.

More than twenty years after the last Mediterranean expedition, Ocean Drilling Program (ODP) sedimentary material is still intensively studied by international research groups. Despite several research vessels (Marion Dufresne, Meteor, Urania) have been carried out widespread cruises and have been collected many sediment cores, the ODP strategy (e.g. in-depth preliminary investigation, multi-core site drillings) is definitively much more suitable for regional palaeoenvironmental and palaeoceanographic reconstructions that need high-quality and high-resolution samples and a long-term time perspective.

I have personally built much of my scientific career on ODP material. More than ten ISI indexed journal papers have been published on the Sicily Channel Site 963. And several research pieces dealing with ODP sediments are actually submitted or in preparation (e.g. Site 967, 968, 975 and 976).

This communication is an acknowledgment to the European Consortium for Ocean Research Drilling (ECORD) and all international partners that funded world-wide campaigns and is also a solicitation to the Italian research ministry to invest adequate funding to preserve the ECORD partnership. This investment is pivotal to keep Italian research competitiveness in emerging scientific issues, such as palaeoclimate and global warming. But, most importantly, the investment is crucial to support the growth of a new generation of young scientists, allowing their participation to leading scientific topics and partnerships.

# Impact of the Early Eocene Climatic Optimum on planktic foraminifera: the crucial record from oceanic sites

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Keywords: Early Eocene Climatic Optimum, Atantic and Pacific Oceanic sites, planktic foraminifera.

The Early Eocene Climatic Optimum (EECO; ~53-49 Ma) is the extended interval of peak Cenozoic global warmth and carbon cycle perturbations. Planktic foraminifera represent an excellent class in which to examine links between this crucial interval of Earth climate and evolution. The record from the oceanic sites provides the essential and unique archive to investigating changes in planktic foraminiferal assemblages across the EECO. Our analysis reveals that the relative abundance of the surface-dweller symbiont-bearing genus *Morozovella* at Atlantic Site 1051 markedly and permanently declined close to the  $d^{13}C$  excursion referred to as "J" event, which marks the beginning of the EECO. The well-preserved material from the oceanic site allowed us to explore through  $d^{13}C$  analyses a possible cause of the morozovellid decline: the loss of photosymbionts. A bleaching episode actually occurred at the start of the EECO but this was transitory thus excluding photosymbiont expulsion as the main cause of the morozovellid decline. Other hypotheses to explain this change may include the morozovellids and acarininds biological differences in tolerance to temperature and ocean chemistry, such as pH, that reduced morozovellid resilience and caused threshold crossing for their thriving. For instance, reproduction of most morozovellids that sank slightly deeper in the mixed-layer differently from most acarininids, may have been hindered by warmer temperatures. At South Atlantic Site 1263 the morozovellid decrease is delayed by ~165 kyr, suggesting that unfavourable conditions for morozovellids occurred at lower latitudes first. At Site 1263 major changes across the EECO occur also in other, minor genera. These changes consist in a virtual disappearance of biserial chiloguembelinids and a marked reduction in the abundance of subbotinids. As these genera are linked to the sub-surface waters and thermocline, we interpret the environmental changes across the EECO as related to subsurface warming. The record from the oceanic thus enables to demonstrate that the EECO impacted the entire upper water-column and produced contraction of ecological niches. Our data demonstrate that the Morozovella decline in abundance was geographically widespread as it is recorded at the EECO beginning also in subtropical Pacific (Site 577) and in the Atlantic equatorial Site 1258. The impact of the EECO on morozovellids involved also shifts in the coiling preferences of Morozovella that changed from prevailing dextral to sinistral coiling direction as recorded at Sites 1051 and 1263. Previous interpretations of coiling flips in planktic foraminifera in the early Eocene, especially including morozovellids, have favoured a genetic explanation rather than an ecological response. Our present data cannot validate or disprove this idea, but stimulate renewed thought on the matter.

#### Contribution of thermochronology to marine sediments study in Antarctica: insights into mountain uplift, basin history and ice-flow patterns

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Keywords: thermochronology, Antarctica.

In the last 20 years, the Ross Sea Embayment has been the target of several drilling campaigns, carried out by an international consortiums with the involvement of the DSDP-ODP program,

During the last decade, the application of thermochronology to the study of marine records in Antarctica has been extensively implemented. The first application of dates back to the study of the ANDRILL drill core. Since that time, a group of Italian researchers emerged such as a leader in the application of the thermochronology to the marine record in order to reconstruct climatic and tectonic history.

Detrital thermochronology, often coupled with petrography and other geochronological tools, provides valuable information about rock source of sediments, its location and exhumation history. Sediment provenance can be therefore reconstructed and, in turn, pattern of the glacial flow can be determined.

Our thermochronological studies were initially focused on samples from the two ANDRILL and Cape Roberts Project wells (Zattin et al., 2010; 2012; Olivetti et al., 2013). Main results shed light on the variations of the source rock that seem related to the fluctuations of the Ice Sheet trough time as far back as the early Oligocene, when the existence of a Ice Sheet is under debate.

Recently, we enlarged the study area to the eastern Ross Sea (Perotti et al., 2017) to study the dispersal pattern of the Last Glacial Maximum sediments and to discriminate the West Antarctic Ice Sheet source and the Eastern source. The identification of the different contributes in the past by the two Ice Sheets was also the target of the work on DSDP 270, 271, 272 drill cores (Balestrieri et al., 2012). Currently, our thermochronological analysis are focused on Pliocene record of the CIROS wells (Li et al., 2018).

IODP interest is currently focused on Antarctica, where expedition 374 has been recently carried out and other expeditions are planned. The possibility to perform detrital thermochronology might provide relevant contributions for provenance analysis and ice-flow pattern reconstruction.

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# The importance of the scientific ocean drilling for a micropaleontologist: experiences from six ODP/IODP Expeditions

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Keywords: ODP-IODP Expeditions, high-quality sedimentary successions, high-quality biostratigraphy and biochronology.

The opportunity to be involved in scientific ocean drilling programs has been an experience that greatly enhanced my expertise and helped, and improved, my scientific career. In a timeframe of 18 years, I participated in five Ocean Drilling program (ODP) Legs in the Atlantic and Pacific oceans as nannofossil palaeontologist and sailed again, for the sixth time, on the R/V JOIDES Resolution in 2009, as co-chief-scientist of IODP Expedition 320/321 in the eastern equatorial Pacific. The work on board an IODP cruise is a special experience for a geoscience researcher for several reasons: it rarely happens to be part of a group of diverse researchers all working on the same "problem" at the same time, all dedicated to a project for which they exchange their knowledge and expertise with the common purpose of successfully completing the expedition. It also represents the amazing experience of carrying out and completing a research program in "real time": from getting the samples, processing them, analysing and obtaining results, a project that involves most of the geoscience disciplines develops in just the two-month-timeframe of a typical ODP-IODP expedition. As for the drilling expeditions I participated, that were all focused on paleoceanographic-paleoclimatic themes, the high-quality sediment cores recovered represented the suitable material for generating excellent micropaleontology data in different intervals of geological time. This was achieved through the improvement of database that, for my research field on calcareous nannofossils, resulted in high-quality biostratigraphy with its potential for high resolution calibration of biohorizons to the other records used for dating, as isotope stratigraphy and orbitally tuned cyclostratigraphy. Moreover, the obtained excellent data originated an accurate database on ancient nannofossil communities that provided information useful for clarifying their paleoecological affinities and possible paleoenvironmental meanings, and for describing the evolutionary "behaviour" of nannofossils during prominent climatic episodes and critical climatic transitions. A learned lesson from this special experience is properly described as follows: "...any geologist who looks further than the head of his hammer or the stage of his microscope will also have to take the wide oceans within the circle of his view." (Keunen, 2002).

Kuenen, P.H. (2002): No geology without marine geology. Int. Jour. Earth Sciences, vol. 91, 54-61.

# SW Indian Ridge Lower Crust and Moho; Expedition 360 Post-Cruise Meeting (14-19 May 2018, Siracusa, Italy)

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Keywords: IODP, Atlantis Bank, Post-cruise meeting.

International Ocean Discovery Program (IODP) Expedition 360 represents the first leg of a multi-phase drilling programme ('SloMo' project) aimed at investigating the nature of the lower crust and Moho at slow spreading ridges. As an initial phase, IODP Exp. 360 intended to recover a transect of the lower oceanic crust formed at Atlantis Bank, an oceanic core complex on the SW Indian Ridge. During this expedition, 89 cores of gabbroic rocks were recovered at Hole U1473A, drilled to 789.7 m below seafloor, subsequently deepened to 809.4 mbsf during transit Expedition 362T. Between 14 and 16 May, we hosted the Expedition 360 Post-Cruise Meeting, with the support of IODP-Italia. Held in the historical city of Siracusa, 40 scientists from the science party and shore-based collaborators presented the result of ongoing research in 23 oral and 8 poster presentations. The sessions included igneous and metamorphic petrology, geochronology, geochemistry, palaeomagnetism and microbiology. Preliminary results and intense discussions allowed planning future research activities and new collaborations. After three days of conference, most of the participants moved towards Catania for a field trip to the volcanism of the Hyblean Mountains and the Mt. Etna. Under the guidance of Boris Behncke (INGV, Catania), we observed spectacular volcanic outcrops related to island growth and flood basalt lavas emplacement in the area between the towns of Palagonia and Militello. Basalt pillows, breccias, hyaloclastites and pahoehoe flows units were observed and discussed in comparison with the subaquatic activity commonly observed at Mid Ocean Ridges. The group then faced towards the Mt. Etna, where, guided by Rosanna Corsaro (INGV, Catania), we visited the summit craters at ~3000 m and several lateral craters along the southern flank of the volcano until the town of Nicolosi. The last day of excursion the group was led to the famous hyaloclastites-pillow lava association located in the town of Aci Castello. The meeting ended with a visit of the INGV headquarter in Catania.

# **IODP Proposal 927-pre: the TyrrhenIan Magmatism & Mantle Exhumation (TIME)**

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Keywords: Drilling, mantle exhumation, Vavilov plain.

The main object of the Proposal 927-pre: "TyrrhenIan Magmatism & Mantle Exhumation" (TIME) is the understanding of the relationship between the exhumed mantle rocks and the overlying basalts sampled in the Tyrrhenian Basin during the previous ODP Leg 107 (Kastens et al 1988).

The scientific objectives of the proposal include studying the kinematics of the opening, the nature and timing of associated magmatism and the geochemistry and deformation of the exhumed mantle section.

The proposal resulted from the outcome of the MagellanPlus Workshop "TyrrhenIan Magmatism & Mantle Exhumation" (TIME) sponsored by IODP and ECORD. The workshop was held in the Institute of Marine Science (ISMAR) of the National Council of the Italian Research (CNR) in Bologna on June 5-7, 2017. The proposal 927-pre was submitted on October. 2017 and received the recommendation for the development into a full proposal by the IODP STEP Panel on February 2018.

The database used to conceive the drilling project is possibly one of the best available from a rifted basin. The basement of the Tyrrhenian basin has been dredged at highs and drilled in several campaigns, and the stratigraphy is reasonably well known from three previous drilling expeditions, DSDP leg 13, DSPD leg 42 and the ODP leg 107 It is available a full-coverage, high-resolution, multibeam bathymetry of the basin as well as a large data set of vintage and modern 2D MCS reflection profiles and seven regional wide-angle seismic profiles crossing the main geological domains (Moeller et al 2014; Prada et al 2016, 2018).

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# **Session S5**

# Onshore and offshore Quaternary sedimentary processes and sequences in the Mediterranean regions

Conveners AND CHAIRPERSONS Sergio G. Longhitano (Università della Basilicata) Francesco L. Chiocci (Sapienza, Università di Roma) Marcello Tropeano (Università di Bari) Domenico Chiarella (Royal Holloway, University of London) Marco Brandano (Sapienza, Università di Roma)

## Deformed stratigraphic markers in the shallow subsurface of the Po Plain: indicators of recent tectonic activity?

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Keywords: Stratigraphic markers, late Quaternary, Po Plain.

Seismic-risk area. In May 2012, an earthquake sequence with two mainshocks of magnitude Mw 6.1 and 6.0, hit this area. These seismic events were generated by the most external thrust systems of the Northern Apennines. These structures, imaged in the industrial seismic lines, are sealed by a thick (up to 6 km) sedimentary infill that accumulated since the Late Pliocene. Seismic reflectors depict a progressively decreasing deformation of sedimentary strata from the deeper to shallower units. The recentmost strata appear nearly undeformed.

We reconstructed the subsurface stratigraphy of the uppermost 50 m, generally beyond the resolution of industrial seismic lines, through the correlation of hundreds of core data and piezocone penetration tests. Our investigation was based on the correlation over tens of kilometers of distinct types of stratigraphic markers, including: paleosols, flooding surfaces, lagoon and peat horizons. These stratigraphic markers were used as possible indicators of recent tectonic activity, as most of them appear folded above the culmination of the buried anticlines.

Pedogenically modified horizons within Late Pleistocene floodplain clays show high correlation potential. Particularly, two weakly developed paleosols were traced south of the Po River (Amorosi et al., 2017): an older paleosol, dated to the onset of the Last Glacial Maximum (LGM) (30-24 cal ky BP), and the Younger Dryas (YD) paleosol, dated to 12.9-11.5 cal ky BP. Differences in elevation of several metres are measured along the LGM and YD paleosols. However, as paleosols may have complex morphologies at time of formation, only a qualitative evaluation of their post-burial deformation was possible.

On the contrary, the Holocene sedimentary succession includes most reliable indicators of post-burial deformation. P representing approximately horizontal surfaces at time of deposition, are also folded above the blind thrusts. The disadvantage of this type of markers is their limited areal extent, restricted to the modern coastal plain.

The geometry of strata that accumulate in proximal-foreland and wedge-top basins can provide clues to the rates of deformation resulting from combined tectonic activity, flexural subsidence and sediment compaction. Similarly, the deformation of the Late Pleistocene and Holocene markers in the Po Plain may have been driven by the combination of: (i) tectonic activity along the Apennine blind thrusts and (ii) differential subsidence driven by compaction of the underlying sediments. This study provides first insights on strata deformation at intermediate time scales (103-102 y). Such scales are crucial for the calculation of slip rates in selected fault systems, especially in the case of long earthquakes recurrence times. Quantifying the contribution of sediment compaction to strata deformation is the next step of this research project.

Amorosi, A., Bruno, L., Cleveland, D. M., Morelli, A. & Hong, W. (2017). Paleosols and associated channel-belt sand bodies from a continuously subsiding late Quaternary system (Po Basin, Italy): New insights into continental sequence stratigraphy. Bulletin, 129(3-4), 449-463.

# Braid-Delta Depositional System in Peri-Adriatic Basin, Italy

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Keywords: Pleistocene, delta-facies, per-adriatic basin.

Braid-Delta depositional system is widely developed in the "Colonnella foothills" area (Adriatic coast, northern Abruzzi region, central Italy). this study illustrates the braid-delta depositional system in terms of facies sequence and association. Three different facies associations have been distinguished in Colonnella delta sequence: delta plain, delta front, prodelta/offshore. The uppermost part of the Colonnella delta sequence is composed of overbank deposits, while muddy prodelta deposits form the lowermost part of the sequence. Crevasse splays, levees, bays, or abandoned channels occur in the delta plain. The delta front and upper prodelta are occupied by distributary mouth bars. Distal bar and bar front deposits of the distributary mouth bars have a distinct upward-coarsening sequence. Beach facies (foreshore, shoreface) are developed in the delta front to upper prodenta. Tidal influence consisting of wavy bedding and herringbone cross-lamination, often formed in the tidal bar deposits. The prodelta/offshore deposits are caractherized by dark-gray, massive or faintly bedded silty mudstone alternated to veri fine-grained sandstone beds, containing marine macrofossils and abundant microfauna composed maily of planktonic and benthic microfossils, including foraminifera and nannoplankton. Bioturbation and burrows also occur. Reddish silty-clay beds bounded at the top by erosive surfaces (paleosoil), indicate times of subaerial exposure and weathering processes.

# Morpho-stratigraphic characterization of a submarine deltaic system linked to the Mazzarrà River in the Gulf of Patti (Southern Italy)

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Keywords: hyperpycnal flows, seismo-stratigraphy, gullies.

The recent collection of high-resolution multibeam bathymetry and high-resolution seismic profiles in the Gulf of Patti has revealed the presence of pro-deltaic deposits on a 6-km-wide shelf along of a sector of the tectonically-controlled NE Sicilian margin (southern Tyrrhenian Sea; Casalbore et al., 2016). These deposits are linked to the mouth of the Mazzarrà River, having a length of about 25 km, a drainage area of ca. 120 km<sup>2</sup> (maximum elevation around 1200 m) and average slope gradients of 5°. This river is also characterized by a torrential regime, with flash-floods able to transport a large amount of sediment into the sea in very short time-span. The submarine prodeltaic deposits are morphologically characterized by waveforms trending overall along strike and incised by cross-strike gullies of variable length. The gullies can be interpreted as the erosive trace left by the passage of hyperpycnal flows on the seafloor, whereas the genesis of the waveforms is more complex and could be associated to erosive-depositional processes associated to these hyperpycnal flows or incipient instability processes (i.e., creep). Seismic data show that the prodeltaic system developed after the Last Glacial Maximum at 20 ka and allow to divide it in different seismic units that can be associated to the transgressive and highstand system tract. In this work, we discuss the role of riverine and marine processes during the entire post-glacial evolution of this prodeltaic system.

Casalbore, D., Ridente, D., Bosman, A., Chiocci, F. L. (2017): Depositional and erosional bedforms in Late Pleistocene-Holocene pro-delta deposits of the Gulf of Patti (southern Tyrrhenian margin, Italy). Marine Geology 385(2017) 216-227.

# Submarine depositional terraces in the Mediterranean Sea: Sgenesis and their possible use as proxy for paleo-sea level reconstructions and neotectonics

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Keywords: prograding wedges, sea-level, tectonically-controlled margins.

In the last few decades, a growing attention has been focused on the identification and use of submarine geomorphic/stratigraphic markers to estimate past sea levels and vertical movements, such as submerged paleoshorelines, paleo-coastal cliffs and barrier beaches, offlap breaks of continental margins, outer edges of reefless insular shelves on volcanic islands and sand-rich submarine prograding wedges (also named infralittoral prograding wedges or submarine depositional terraces). These latter features are depositional bodies commonly recognized in high-energy marine settings (i.e. tectonically-controlled coast and insular volcanoes), such as along the Italian coastlines. A first atlas of such features was realized by Chiocci et al. (2004), mostly based on high-resolution seismic profiles. This methodology allowed to image their inner geometry but was not suitable for reconstructing the lateral continuity of these bodies, often changing at short distances on active continental margins. This problem was recently solved using multibeam bathymetry, that allows an accurate and detailed mapping of shallow-water areas, so providing the possibility to better define the 3-D geometry and depth of these depositional bodies (Casalbore et al., 2017). In this work, we present several examples of submarine depositional terraces from different locations in the Tyrrhenian Sea aimed at discussing the main factors that control their formation and preservation as well as their possible use as a proxy of past sea-levels and neotectonics.

Casalbore, D., Falese, F., Martorelli E., Romagnoli, C., Chiocci, F.L., (2017): Submarine depositional terraces in the Tyrrhenian Sea as a proxy for paleo-sea level reconstruction: Problems and perspective. Quat. Int. 2017, 439, 169-180.

Chiocci, F.L., D'Angelo, S., Romagnoli, C. (2004): Atlas of Submerged Depositional Terraces Along the Italian Coasts. In: Memorie Descrittive della Carta Geologica d'Italia, vol. 58.

# "Spatio-temporal channel changes, in a Basento river reach (south Italy), in response to the great flood events of 2011 and 2013, with the application of Event Dynamic Classification (EDC) and Event River Morphodynamic Corridor (EMCo)"

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Keywords: flood event, planimetric changes, morphological impacts.

On March 1<sup>st</sup>, 2011 and from 1<sup>st</sup> to 3th December 2013, the Basento River (south Italy) was affected by significant flood events with an estimated return interval ranging from 30 to 50 years the first event and 100 years the latter (source basin authority of Basilicata region). This study investigates the morphological responses of a reach of the Basento River to these major flood events in order to document planimetric changes (width and morphological pattern) which occurred in response to the floods, comparing this response with historical planimetric changes trend of last 150 years, the Event Dynamic Classification (EDC) and Event River Morphodynamic corridor (EMCo) preliminarily evaluated for the reach. The analysis of EDC and EMCo, which belong to the "Methodological framework for hydromorphological assessment, analysis and monitoring (IDRAIM)" (Rinaldi et al., 2016), allow to investigate possible channel dynamics associated with extreme flood events (i.e.>100 years return period) (EDC) and to delineate the areas of such fluvial morphological dynamics associated to extreme flood event (EMCo). Along the entire reach studied (about 4 km long) was observed a significant channel widening of 30% and 40%, of the preflood channel width, respectively for the 2011 and 2013 flood event. The assessment with the historical channel width variability, over the last 150 years, has confirmed that both channel width variation are amply included in the historical range of channel width variability. Changes intensity in channel width is in line with EDC analysis, which has defined with an "High" class the reach studied, that means very strong morphological variations degree expected. Finally, areas involved in dynamics channel changes, due to the floods, are completely included in EMCo defined for the reach.

Rinaldi, M., Surian, N., Comiti, F., Bussettini, M. (2016): IDRAIM - Sistema di valutazione idromorfologica, analisi e monitoraggio dei corsi d'acqua - Versione aggiornata 2016 - ISPRA - Manuali e Linee Guida 131/2016. Roma, gennaio 2016.

# Late Quaternary paleoenvironmental evidences from benthic foraminifers in the Pontine Archipelago shelf (Tyrrhenian Sea, Italy)

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Keywords: benthic foraminifers, Quaternary, Pontine Archipelago.

Two cores were collected by a gravity corer, during the cruises "Urania 2001" and "Urania 2004" carried out by R/V Urania offshore Ponza Island. They were recovered at 60 (CS1) and 122 m water depth (Caro1) and are 218 and 69 cm long, respectively. The lithological description of the cores was carried out at the time of cores sampling. A total of 32 samples (consisting of a 1 cm thick sediment slice) were collected generally every 10 cm: 25 samples from the core CS1 and 7 from the core Caro1 The core bottoms have AMS radiocarbon ages of 9672±168 cal yr BP for CS1 and 16012±223 cal yr BP for Caro1.

The lithology of the core CS1 is represented mainly by coarse to fine clayey sands. The lower part of core CS1 (-218 cm to -176 cm) is composed of coarse sands, rich in bioclasts and centimetric rhodoliths. The upper part (from -176 to the top) is composed of fine clayey sands with the presence of thin layers of coarse bioclastic sediment between -142 and -43 cm. The benthic foraminiferal assemblages are fairly constant along the core, with the dominance of *Asterigerinata mamilla* and *Lobatula lobatula*. They are typical species which dominate the recent sediments of Pontine Archipelago, between 30 and 100 m wd.

The core Carol consists of coarse sands in the lower part, passing upward into more fine and clayey sands. From the bottom (-69 cm) to -55 cm coarse sands with abundant rhodoliths are present; from -55 cm to -34 cm, silty sands are found showing abundant bioclasts (e.g., rhodoliths and molluscs). The upper part (between -34 and -15 cm) is composed of coarse sand, with abundant bivalves, rhodoliths and bryozoans. Finally, to the top fine sand rich in small bioclastic fragments was found. In this core, a clear change of benthic foraminiferal assemblages was recognised at -25 cm: from the bottom to -25 cm, the foraminiferal assemblage was dominated by *Lobatula lobatula* and *Asterigerinata mamilla*; between -25 cm and the top, the assemblages were characterised by a species typical of deeper environments (100-200 m wd) such as *Cassidulina carinata*.

For core CS1 benthic foraminiferal assemblages and AMS radiocarbon dating indicate that the cored interval represents the Holocene portion of the stratigraphic succession. For the deepest core (Caro1), the sharp transition from coarser to finer lithology, together with the change from a shallow benthic foraminiferal assemblage to a deeper assemblage, suggests that the its bottom was deposited during the early stages of the last sea level rise. Based on these data the bottom of the studied cores represents the upper circalittoral zone (50-100 m wd), where coralline red algae reach the maximum abundance and distribution in the Pontine Archipelago.

# Quaternary transgressive, tidal- and wave-dominated coastal-systems in the northeastern Sardinian relict shelf: spatial and temporal variations in coastal process regime

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Keywords: estuary, barrier island, lagoon.

Most of the modern coastal areas are mixed-energy environments with spatial changes of dominant processes. In addition, temporal variations in the relative intensity of tidal, river and wave processes, at a range of time scales, have been documented in individual coastal systems. Outcrop and subsurface studies of such temporal and spatial variations in coastal environments are often complicated and mostly incomplete. On the contrary, the study of relict shelf portions can facilitate the complete reconstruction of coastal system evolution during the last sea-level rise. Here, we present such a study, through the interpretation of multibeam bathymetry and Chirp profiles, on the northern Sardinian relict shelf.

Tidal- and wave-dominated sectors were developed at the same time in different portions of the investigated area. Wave-dominated coastal systems prevail in the north, where three coastal barrier systems developed at progressively shallower depths during the last rise of sea level. They bounded tidal basins opened to the north, where tidal channels and bars developed. Tidal inlets and tidal deltas are present in between the single barrier islands. In the southern area, a barrier island system was initially in continuity with the northern one. It enclosed a large basin with tidal bars and channels. Successively, the barrier was reworked by tidal currents and elongated bars and channels formed within a tide-dominated estuary. With continuing sea-level rise, a further barrier formed landward, and enclosed a wave-dominated estuary with tidal channels and bars.

Our study shows that, as a result of the spatial variations of controlling processes, synchronous coastal systems with variable degrees of wave- and tide- domination can develop. Our study also shows that the relative importance of tide and wave processes can vary in time due to oceanographic and morphologic changes inherent to sea-level rise. In particular, our results show that tide-influenced deposits can be an important constituent of coastal successions also in small bodies of water with overall microtidal conditions, such as the Mediterranean Sea. In general, our results show that sequence stratigraphic models for coastal deposits, which generally assume a regionally prevailing process constant in time, largely overlook temporal and spatial changes in dominant regime.

## Past and present sedimentary dynamics of a tide-dominated passageway: the Messina Strait in the central Mediterranean

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Keywords: Messina Strait, tidal dynamics, sediment zone partitioning.

A geological comparison between the modern and the ancient Messina Strait is presented, aiming at deciphering many unclear aspects on the sedimentary dynamics of the present-day marine passageway by using the sedimentological signature preserved in the lower Pleistocene onshore analogue.

The modern Messina Strait, separating the Italian peninsula and Sicily in the central Mediterranean, is dominated by bi-directional, 2-3 m sec<sup>-1</sup> tidal currents, amplified during their passage across the 3-km-wide cross-sectional centre. The tidal dynamics is regulated by semi-diurnal inversions in phase opposition occurring between the interlinked Ionian and Tyrrhenian basins. Tidal flows have a relevant influence on mobile sediments at the bottom, inducing a specific sedimentary zone partition based on the relative position of by-pass and sediment convergence areas. Bed-load pathways, indicated by extensive bedform fields (i.e., tidal dunes), respond to a 'mutually-evasive' mechanism of sediment transport, directed from the centre towards the two opposite strait exits. Recent geophysical (multi-beam) investigations reveal important details on the morpho-bathymetric features of these zones, suggest interplay between tidal currents and other processes (e.g., river floods, gravity flows, storm waves) and clarify the reciprocal role of flood and ebb tidal components in the modern sediment distribution.

During the Early Pleistocene, analogous oceanographic and morphological strait conditions have established in the same area. Nowadays, the onshore margins of the modern strait expose cross-stratified sandstones and biocalcarenites, up to 200 m thick and exhibiting a variety of sedimentary facies with a diffuse tidal signature. Facies analysis carried on a number of stratigraphic sections suggests a strong correspondence between the various ancient deposits with the modern strait environments and confirms the zone partitioning based on the present-day bottom features.

The presented results have a threefold scientific impact: (i) they clarify a number of previously uncertainties on the sedimentary dynamics of the modern strait; (ii) contribute in the reconstruction of the palaeogeographic setting of the ancient Messina passageway; and (iii) add insights for the building of an universally valid depositional model for modern and ancient tidal straits, which are the less well understood among most tidedominated systems.

# Sedimentological and paleoenvironmental analysis of a lower Pleistocene stratigraphic section exposed in the SE Siderno Basin, southern Calabria

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Keywords: Strait, Lower Pleistocene, Calabro-Peloritani arc.

This study documents the sedimentological features of a lower Pleistocene (Gelasian) succession exposed in the south-eastern Siderno Basin (Calabria). The basin is a 50-km-long and 20-km-wide structural depression, developed from the Oligocene to the Quaternary along one of the WNW-ESE-striking shear zone dissecting the Calabro-Pelorani Arc. The investigated deposits represent the uppermost basin-fill interval and include siliciclastic-bioclastic coarse-grained sandstones, exhibiting a variety of cross bedding. These features have been considered as the record of the migration of generations of bedforms in a subaqueous environment under the effect of strong currents. The tidal influence was due to the amplification of water masses, imparted by a coastal narrowing during their transit along the basin, which linked two wider seas (i.e., Tyrrhenian and Ionian). This condition is key to promote conditions for tidal-flow reinforcement in modern settings and can be detected thanks to distinctive sedimentological features (e.g., tidal cross strata) in the rock record.

The studied interval has been associated with a high-energy marine setting based on the exposed ichnofacies. However, it has never been referred to a specific marine depositional environment (e.g., shoreface, offshoretransition, outer shelf, etc. ...). The goal of the present study is thus the identification of a more precise palaeoenvironmental collocation of these deposits within the so-called Early Pleistocene Siderno Strait.

The section is 45.5 m thick and includes fine-grained sandstone tabular cross strata (B1) and biocalcarenitic trough-cross strata (B2), erosionally overlying upper Pliocene shelf marls and fine-grained sandstones. Sedimentary structures consist of angular, tangential and sigmoidal foresets with compound architectures and SSE direction of migration. Internally, plain-parallel and cross lamination, soft-sediment deformations and highly-bioturbated intervals also occur. The most diffuse ichnogenera indicate *Glossifungites* e *Skolithos*. Macro-fossil remains include molluscs, echinoids and bryozoans, whereas thin-section analyses reveal planktonic foraminifera indicating open-marine conditions. Upwards, the succession transits to plain-parallel, highly burrowed bioclastic fine-grained sandstone strata with a scarce or null tidal signature.

Based on these integrated analyses, we suggest an outer shelf environment for the investigated deposits. This area possibly represented the eastern depositional zone of the Siderno Strait, where tidal currents promote the migration of sinuous dunes, whose bioclastic ash was sourced from an *in situ* carbonate factory established thanks to a specific current-dominated hydrodynamics. The upward decreasing of the tidal signal points towards a demise of the tidal circulation in the strait, presumably due to a stage of relative sea-level rise and consequent enlargement of the basinal cross section.

#### The Holocene stratigraphic architecture of the Volturno River delta (Southern Italy)

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Keywords: Campania Plain, Volturno River, Last Glacial Maximum.

The aim of this research is to present a paleomorphological reconstruction of the buried incised valley of the Volturno River, across the coastal region connecting the northern Campania Plain and the Gaeta Bay during the Last Glacial cycle. The study is based on comprehensive set of onland borehole data and offshore reflection profiles and will attempt an interpretation of the Volturno incised valley as an example of a highly dynamic stratigraphic system dominated by volcanic activity during severe climatic changes. The volcaniclastic deposits originated by the Phlegrean Field caldera 39 ka eruption (Campania Grey Tuff - CGT) form the substrate for the Holocene and recent sedimentation.

The digital surface model reconstructed for the upper CGT surface shows a 15-20 km wide Late Quaternary paleovalley incised by the Volturno River into the thick ignimbritic unit. The asimmetry of the southern valley flanks was shaped by the presence of an ancient river (Clanio River), reclaimed during the XVI century, that resulted in the enlargement of the valley and the formation of a complex deltaic system in the southern part.

Correlation of stratigraphic data from the subsurface of the Volturno Plain with sequence stratigraphic interpretation of high-resolution (1kJ sparker) single channel reflection seismic profile offshore the Volturno river mouth indicates that the Volturno buried paleo-valley was likely incised throughout the Late Pleistocene - early Holocene, during the Last Glacial eustatic cycle.

The boundary between the substratum of the paleo-Volturno valley and its sedimentary fill is marked by a well-developed unconformity and associated stratigraphic gap that separates the older Quaternary alluvial deposits and the Campania Ignimbrite (ca 40 ka BP) from the overlying uppermost Pleistocene-Holocene coastal prism entrenching the incised valley. The onset of the sea-level rise, that followed the climax of the Last Glacial Maximum since ca. 15 ka BP, caused marine ingression deep into the Volturno incised Valley and was associated with rapid backstepping and landward shift of depositional systems. Maximum marine flooding conditions are documented at 7,0-6,5 ka BP by the occurrence of prodeltaic deposit, that have been cored between 18 and 25 m beneath the surface. Since the middle Holocene, a progressive lowering of the Post Glacial sea-level rise created conditions favorable to early aggradation (6,5 -4,5 ka BP) and late stage progradation (< 4,5 ka), accompanied by seaward shift of depositional systems. This caused, in turn, a rapid filling of the accommodation space over the former incised valley, with the formation of the modern Volturno alluvial Plain, coastal lagoon and beach barrier system.

# Cyclic sedimentary pulses in the volcanostratigraphic succession of Mt. Etna: evidence for climate-controlled clastic deposition

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Keywords: Mt. Etna, epiclastic deposits, Quaternary volcanostratigraphic succession.

The Late Quaternary volcanostratigraphic succession of Mt. Etna shows distinct epiclastic horizons that mark the major erosion surfaces, separating the volcanic units of different age. We used the analysis of the stratigraphy of the eastern flank of Mt. Etna as a magnifying glass to investigate the climate-controlled variation of the sedimentary supply of the clastic deposition over the time, to be compared with the stratigraphic record of the marine terraces along the Ionian coast of Sicily and the OIT curve. Out of the Etnean area, the Late Quaternary clastic deposition produced few meter-thick highly discontinuous sequences, composed of distinct unconformity bounded wedges, that cumulated at the base of slope. Along the coast, the Late Quaternary clastic wedges form distinct marine terraces due to the generalised tectonic uplift of the region. Within the volcanic successions of Mt. Etna, the clastic wedges have huge vertical lithostratigraphic separations due to the interposition of conspicuous volumes of volcanic products that have been emitted between two consecutive cycles. Moreover, in the volcanic area the rate of supply is largely higher than in the surrounding areas, due to the rapid accumulation of the relief that emphasized the production of clastic material. The study was focused on the huge volumes of epiclastic deposits which are exposed along the main fault scarps of the eastern flank of Mt. Etna and have been drilled in a vast area from Acireale to the village of Santa Venerina. The detailed field mapping, combined with the available radiometric age of lavas and the results of petrochemical analyses of the main lithostratigraphic horizons provided an updated lithostratigraphic scheme of the region, well constraining the timing of the impressive sedimentary imput that interacted with the history of the volcanic activity. Comparison with the OIT and the eustatic curves indicates that the effectiveness of agents on the landscape, driving the maximum rate of transport and deposition, concentrated during the periods of the rapid sea-level rise rather than the entire periods of the sea-level highstands, thus suggesting that the increase of discharge has been strictly related to climate crises induced by the main deglaciation processes.

# **Session S6**

# The dynamics of sedimentary processes in coastal areas

Conveners AND CHAIRPERSONS Massimo Moretti (Università di Bari) Daniela Ruberti (Università di Campania-L. Vanvitelli) Vincenzo Pascucci (Università di Sassari)

#### Late Quaternary stratigraphic architecture of the Volturno coastal plain, southern Italy

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Keywords: Stratigraphic architecture, Late Quaternary, Volturno coastal plain.

The Volturno plain, located along the Tyrrhenian side of the southern Italian Apennines, is a large alluvialcoastal plain developed during Pliocene-Quaternary times. The block-faulting of the western flank of the chain occurred during this period is responsible for its planimetric squared shape. Although the Volturno plain has already been the object of several relevant studies, we will try to define a more detailed stratigraphic and palaeoenvironmental reconstruction before and after the Campania Ignimbrite (CI) eruption and the role of tectonic and eustatic forcing in the evolution of the coastal plain. To this scope, the results of an extensive and detailed stratigraphic analysis of the Late Pleistocene - Holocene infill of the Volturno plain based on almost 700 well logs are here presented. On these grounds, a map of the base and the roof of the CI and several geological cross-sections have been realized by GIS interpolation techniques.

The stratigraphic architecture of the Late Quaternary Volturno plain infill is featured by 7 lithostratigraphic units, which appear sufficiently homogeneous from sedimentological and paleontological viewpoints. Stratigraphic and chronological constraints based on volcanic and marine deposits from literature enable us to propose a general chronology and to attribute age intervals for each unit. Stratigraphic relationships among the units suggest a complex Late Pleistocene - Holocene sedimentary evolution of the coastal-marine to continental palaeoenvironments of the Volturno plain. Further, the reconstruction of the CI base and roof allowed upgrading the 3D shape of the Volturno plain palaeomorphology before the deposition of Upper Pleistocene - Holocene sediments. An asymmetrical shape of the ancient morphology of the plain - with a steeper slope toward the north-west border - and the lack of coincidence between the present course of the Volturno River and the main buried bedrock incision are inferred.

The Late Quaternary evolution of the Volturno plain appears mainly controlled by eustatic changes of the sea level during which intense volcanic activity occurred. The rapid sea-level rise after the LGM is testified by a backstepping depositional architecture of the Holocene deltaic-coastal and lagoonal-swamp systems directly on the largely incised Late Pleistocene palaeo-Volturno plain. The maximum ingression of the shoreline was about 3-4 km inland. Starting from 5 ka B.P. ca., in response of the decreasing rate of sea level rise, a coastal and delta system progradation and alluvial aggradation are documented. Taking into account also the subsidence data, Late Quaternary tectonics should be considered active to produce the asymmetry of the CI roof as well as the lateral migration of the Volturno River during this time-span. A similar trend seems to persist in more recent times, as suggested by the presence of a thick alluvial succession located to the south of the present-day main channel.

# Evaluate the effectiveness of renaturalization processes in a dune system: input from a multi-method analysis of shoreline evolution in South Sicily, Italy

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Keywords: Coastal erosion, erosion rate, photogrammetry.

In Italy, nearly 37% of the coastlines had been affected by erosion more than 10 meters from 2000 to 2007 and the phenomenon is largerly widespread and seems not decreasing (ISPRA, 2012). In the past, the protection methods implemented against erosion were hard, short lived, expensive and not eco-friendly, as precast reinforced concrete units placed to reduce the erosional power of wave and tide. Today, the attention has been shifting towards soft, but pro-active methods which are cheaper and reasonably address the root cause of the problem without much "side-effects", and many non-traditional ways to restore beaches, including the use of geotextile sand-filled bags, green belts, bio-engineering, beach-face dewatering system, are being used.

The present study evaluates the erosion trend on short/medium and long term of the shoreline between Licata harbour (AG) and Gela harbour (CL) and the state of the art of the soft and pro-active erosion mitigation methods in Punta Braccetto (Santa Croce Camerina - RG). These areas belong to the same physiographic unit, but the former is affected by erosion due to the high anthropization, in the latter there's a dune system in good condition and in which renaturalization measures have put in place.

The analysis includes a diachronic comparison of aerial, satellite photographs and historical, thematic maps, using Digital Shoreline Analysis System, DSAS (Thieler et al., 2017), which calculates shoreline rate-ofchange statistics from multiple historic shoreline positions. We also take in account hydrological and sea data and hydrographic basin ones, sedimentological characterisation has been performed to delineate the evolution of beach morphological elements (Devon et al., 2016). Therefore, using an integrated methodological approach based on determination of shoreline fluctuations, coastal dynamic and beach sedimentological surveying, we want to highlight the effectiveness of renaturalization processes in Punta Braccetto dune system.

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#### Coastal monitoring system to evaluate morphodynamic response on Levanto Bay (Liguria)

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Keywords: beach survey, camera system, sediments transport.

In last year many studies have been conducted to evaluate morphodynamic behavior along the coastline. Instrumental beach survey has been supported by sensors, capable of simultaneously monitoring the water surface displacement due to wave along with the associated flows and sediment suspension (Davidson et all., 2006).

This contribution describes a coastal monitoring assessment (2016-2018) relies upon two sources: camera system and beach survey dataset. Investigation has been conducted on Levanto beach, located on Western Mediterranean sea on the eastern coast of Regione Liguria, Italy. Video monitoring system was installed on the beach at 30 m above Mean Sea Level (MSL) and images were elaborated using the dedicated software BeachKeeper\_Plus, which is an image management and elaboration software which provides Time-Exposure and Variance images (Brignone et al., 2012). Simultaneously, topographic and bathymetric surveys took place during monitoring project; moreover, Grain size beach analysis was performed on seventy samples.

To evaluate morphodynamic response to climate wave, Meteocean Wave Hindcast was employed from October 2016 to March 2018. MeteOcean group at DICCA has developed an hindcast analysis for the period 1979-2018 for the whole Mediterranean basin (Mentaschi et al., 2015).

Obtain results prove which remote video recording paired with survey data is useful to understand wave impact on investigated area. Indeed, video monitoring image analysis and surveyed data establish a long shore sediments transport from West to East, producing a volume increase on eastern sector of the bay. Time-exposure and Variance methods are able to identify cross-shore and long-shore flow along coastline. In summary: 1)recorded images detected suspended sediment transport, 2) beach surveys identified bed sediment transport and 3) grain size analysis supplies sediments arrangement from the inshore to backshore. In both cases, climate wave from SW is dominant and coastal structure plays a fundamental role on morphodynamic behavior. Employment of this two methods provides a complete view of main hydro-morphodynamic features of Levanto beach.

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#### Anthropogenic effects on coastal erosion in south Sicily: the case history of Pozzallo coastline

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Keywords: Coastal erosion, dune system, sedimentary balance.

The present work is focused on the study of shoreline advancement and recession of the coastal area between Pozzallo (RG) and Santa Maria del Focallo (RG) and on the observations of the environmental transformations which occurred from 1880 to 2016, in order to identify main causes of the problem and find and suggest the most appropriate solution to local entities. The study combined the sedimentological characterisation of the beach and the comparison of shoreline in historical and technical maps and aerial and satellite photographs. The coast is divided in 14 transepts, traced perpendicular to the 1928 coastline, used as zero line, and in correspondence of which shoreline rate-of-change is calculated. Moreover, we outlined natural and anthropogenic elements, as dunes, quagmires, infrastructures, in every maps and photos with the aim of recognizing the environmental changes. The diachronic analysis highlights a shift line speed between 2,6 m/y and -2,6 m/y and a range of shoreline advancement/recession between -130,5 m e 107,3 m. Specifically, it has shown that Pozzallo shore has been increasing of several meters in the last thirty years, due to the construction of the commercial and touristic harbour. At the same time, Santa Maria del Focallo beach has been affected by high erosion, because of Pozzallo harbour contribution to the reduction of solid transport from the west and of disappearance of dune system, destroyed by the rising urbanization of the coast. Other two events negatively affected coastal ecosystem in the study area: the reclaim of the numerous quagmires and the building of a coastal road, the SP 67, alongside the shore. The increasing urbanization and anthropization significantly altered the dynamic balance of the shore. Clear guidelines on the approach to tackle the problem are provided by the European Parliament in the Integrated Coastal Zone Management (GIZC) in Europe (European Council, 2002), which advises the need, on one hand, to promote integrated use of the coast, decreasing unauthorised building, and, on the other hand, to restore natural shore refilling, furthered by renaturalization of the dunes.

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#### Provenance and dispersion of heavy minerals in the beach sand of the Apulia coast

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Keywords: Volcanic Minerals, Mt. Vulture, Coastal erosion.

A peculiar aspect of Apulia beach sand is the occurrence of important amounts of heavy silicate minerals (mainly pyroxenes, garnets and amphiboles), forming thin, dark layers and placers interbedded with the dominant light carbonaticlastic fraction. A granulometric, compositional and microanalytical study was carried out on the sand of the beaches from the Gulf of Manfredonia to the Otranto promontory, in order to detail provenance and dispersion of the heavy silicate fraction. The rocks outcropping along the Apulia coast are mainly represented by the limestones of the Mesozoic platform of the foreland domain and by the Plio-Pleistocenic sedimentary covers. The origin of the silicate minerals cannot therefore be found in the rocks outcropping in the area, but must be related to a more distant source. The Ofanto river, whose mouth is south of the Gulf of Manfredonia, is the main stream feeding the Apulia coast with sediments eroded by the southern Apennines units and the Mt. Vulture volcano. The microanalytical study revealed that the composition of the pyroxene, melanite garnet and Mg-hastingsite amphibole is identical to that of the same minerals found in the sediments along the Ofanto river and occurring inside the volcanic bedrock of Mt. Vulture. A minor population of colorless garnets can be probably related to the recycling processes from the Oligo-Miocene sandstones of Southern Apennine terrains. Heavy detrital minerals shed by Mt. Vulture have been found in the sandy fraction dispersed both northward and southward of the Ofanto mouth. This is in accordance with a main longshore current depositing them in the Gulf of Manfredonia. Part of the sand, however, is transported southward by the littoral currents of the Adriatic Sea. The sandy heavy minerals fraction is not constant along the coastline. The highest contents are in the northern sector, from the Gulf of Manfredonia to Trani, while they almost disappear in the central sector between Molfetta and Torre Canne (BR). South of Posticeddu (BR) the amount of heavy minerals increases again, though being always subordinate to the carbonaticlastic fraction. These variations may be correlated to the coast physiography: the northern and southern sectors are characterized by a larger platform with a wide surf zone and low energy of the waves, while in the central sector a narrower platform is responsible of a higher energy environment, preventing the deposition of the heavy fraction. A coarser grain size also characterizes the beaches of this sector. At a smaller scale, local variations in the heavy minerals abundances are also related to erosional processes due to anthropic factors: an example is the harbor of Margherita di Savoia, whose eastern pier obstacles the northward transport of the Ofanto sediments. The beach southward of the pier has relatively low heavy mineral percentages, while northward the carbonate erosion indirectly causes an enrichment in this component.

#### The textural features of sandy beaches along the Apulian coast

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Keywords: sandy beaches, sedimentary dynamic, coastal erosion.

The Apulia Region (Southern Italy) contains about 900 km of coastal sectors, which corresponds to 12% of the Italian littorals. Most of the economic and social activities are related to the coastal areas (fishing, transports, etc.) and the tourist facilities are concentrated in the coastal localities. Among all the different coastal types, sandy beaches are the most common (more than 650 km in length) since cliffs and rocky shores only give <sup>1</sup>/<sub>4</sub> of the littoral sectors. Therefore, the coastal erosion is one the most potential threats for the economic development of the Apulia Region.

In addition, the Apulian sandy beaches show a large variability, which is characterised by different sedimentological and ecological parameters of the Ionian and Adriatic coastal areas. This variability mainly depends on both variables coastal dynamics and terrigenous/bioclastic supply. In this study, we try to describe some present-day Apulian sandy beaches by using a limited set of quantitative parameters.

To purpose this aim, three different sandy beaches from Apulia coast have been chosen: Torre Canne (Brindisi) and Alimini (Lecce) on the Adriatic coast and Porto Cesareo (Lecce) along the Ionian coast. Sampling procedures were carried out through diving techniques from foreshore to lower shoreface environments (local wave base is about 6 m).

The grain-size analysis allowed us to calculate the statistical parameters of sands with unimodal distribution. The beaches characterised by erosive phenomena were represented by well sorted sands with high kurtosis and negative skewness values, whereas stable beaches were related to poorly sorted sands with lower kurtosis and positive skewness values. The relationship between the main statistical parameters (mean versus kurtosis, kurtosis versus sorting, kurtosis versus skewness) was used to establish the erosive or stable-prograding tendency of the beach.

The most frequently occurring size class of the statistical distribution was analysed with a binocular optical microscope to evaluate the sands composition in quantitative terms. Therefore, the classification of sands included quarts, feldspar, carbonate grains and other components (pyroxene, amphibole and opaque minerals). Within the carbonates class, the percentage of bioclasts was also evaluated. The shell fragments quantity was variable among the different beaches and a bioclasts percentage variability could be defined at different water depths.

The grain-size distribution and the mineralogical compositional of the beach sands are significant data to obtain the evolutionary beach tendency and to establish quantitative textural parameters that can be used for comparative procedures in nourishment interventions.

## The use of mineral interfaces in sand-sized volcanic rock fragments to infer durability

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Keywords: durability, epiclastic fragments, interfacial boundaries.

The use of mineral interfaces, in sand-sized rock fragments, to infer the influence exerted by durability on the generation of sediments, has been determined for plutoniclastic sand (e.g., Heins, 1995; Caracciolo et al., 2012; Weltjie et al., 2018). Conversely, for volcaniclastic sand, it has received much less attention, and, to our knowledge, this is the first attempt to make use of the volcaniclastic interfacial modal mineralogy of epiclastic fragments, to infer durability control at modern beach environment. Volcaniclastic sand was collected along five beaches developed on five islands (Alicudi, Filicudi, Salina, Panarea and Stromboli) of the Aeolian Archipelago, whereas one was sampled near the crateric centre of Stromboli volcano. Each sample was sieved and thin sectioned for petrographic analysis. The modal mineralogy of the very coarse, coarse and medium sand fractions was determined by point-counting of the interfacial boundaries discriminating 38 types of interfaces categories, both not-isomineralic and/or not iso-structural (e.g., phenocryst/glassy groundmass) and iso-mineralic, inside volcanic lithics with lathwork and porphyric textures. A total of 47386 interfacial boundaries have been counted and, the most representative series of interfaces, from the highest to the lowest durability, can be grouped as follows:

a. ultrastable interfaces

Plagioclase/Glassy groundmass»Pyroxene/Glassy groundmass»Olivine/Glassy groundmass»Plagioclase/ Microlitic groundmass»Plagioclase/Pyroxene»Pyroxene/Opaque»Opaque/Glassy groundmass»Plagioclase/ Opaque

b. stable interfaces

Pyroxene/Olivine»Plagioclase/Olivine»Hornblende/Glassy groundmass»Pyroxene/Microlitic

groundmass»Opaque/Microlitic groundmass»Hornblende/Opaque»Olivine/Iddingsite»Hornblende/Plagioclase c. moderately stable interfaces

Hornblende/Pyroxene»Iddingsite/Glassy groundmass»Olivine/Microlitic groundmass»Biotite/Glassy groundmass»Iddingsite/Pyroxene»Iddingsite/Plagioclase»Biotite/Opaque»Olivine/Hornblende and d. unstable interfaces

Opaque/Olivine»Hornblende/Microlitic groundmass»Biotite/Plagioclase»Biotite/Pyroxene»Olivine/ Biotite»Biotite/Hornblende»Rutile/Glassy groundmass»Rutile/Microlitic groundmass.

Grains, eroded from the volcanic bedrock, if affected solely by abrasion, developed a rounded and smoothed form, with prevailing not-isostructural interfaces such as Plagioclase/Glassy groundmass, Pyroxene/Glassy groundmass and Olivine/Glassy groundmass interfaces. Grains that during transport suffered fracturing and percussion have a sharp and angular form: this combined transport mechanisms produce mainly iso-structural interfaces such as Plagioclase/Plagioclase, Pyroxene, Hornblende/Hornblende, and, to a lesser extent, Biotite/Opaque and Biotite/Glassy groundmass interfaces.

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#### The Sabellaria worm reef along the Italian Coast

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Keywords: Sabellaria, worm reef, bioconstruction.

*Sabellaria* is a genus that is included into the Sabellariidae family; it is able to build reefs composed by tubes made up of sand and shell fragments, which are held together with a very strong glue produced by the worm itself. These marine polychaete are commonly called "sandcastle worms" or "honeycomb worms". Under a specific set of environmental conditions, *Sabellaria* can form reefs (consisting of hundreds or thousands of worm tubes) that can vary in thickness, size and patchiness. The more developed reefs form in areas with a large and continuous supply of sand, turbulent water, nutrient availability and mixed rocky/sandy seafloor. Two species of the Sabellaria genus are widespread along the Atlantic coasts of Europe: *S. spinulosa* (Leukhart, 1849) e *S. alveolata* (Linnaeus, 1767).

In the Mediterranean area, *S. alveolata* builds some large reefs, while *S. spinulosa* only encrusts the hardsubstrate with isolated tubes. We have compared the data coming from the first *Sabellaria spinulosa* reef in the Mediterranen Sea (northern Gargano coast, Adriatic Sea, southern Italy) with the main sedimentological features of a well-known reef of *Sabellaria alveolata* along the Tyrrhenian coast (Ostia).

The study of the reef was carried out at various scales: from the mapping of the regional distribution of the *Sabellaria* reefs to the microscopic textural, morphometrical and mineralogical features of the sand grains that are trapped in the tubes. In this work, we describe the results of the SEM and microtomography analyzes carried out on samples collected during seven years of monitoring on the two *Sabellaria* reefs. Similarities and differences between the reefs built by *Sabellaria spinulosa* and *Sabellaria alveolata* are discussed in this work.

#### Roundness controls on modern beach sand from Aeolian Islands

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Keywords: Aeolian islands, beach, volcaniclastic sand.

This work focuses on the textural analysis of 67 modern sand sampled from beaches of the Aeolian islands, and from one sample near the crateric centre of Stromboli volcano, to evaluate the factors that control detrital grain rounding during torrential-type and at beach environments transport mechanisms (Morrone, 2018). A total of 400 points was counted for each thin section of the sand samples, under polarizing microscope, and change in grain roundness degree was assessed to evaluate grain durability to transport. Variations in mean roundness were determined on medium-sand size assigning, to each category of grain roundness, a numerical value ranging from very angular (1), angular (2), sub-angular (3), sub-rounded (4), rounded (5), to well-rounded (6) categories, using a modified petrographic technique proposed earlier by McBride and Picard (1987).

The most common roundness category of sandy grains from Panarea and Stromboli islands is 2 (angular), followed by 3 (sub-angular), 1 (very angular), 4 (sub-rounded), and then with a very low occurrence of 5 (rounded), but lacking 6 (well rounded) grains categories. The sand samples from Alicudi, Filicudi, Salina, Vulcano and Lipari islands show an higher percentage of sub-rounded category (3). Salina, Lipari and Vulcano have the most rounded grains and Vulcano has the highest well rounded percentage of grains among all of the islands coastal sands. The mean roundness of all the analyzed grain types is considerably higher in the east than the west sides beaches, and with a roundness increase from north-west to east. On Aeolian islands, wind and wave energy, decreases from west to east (e.g., Cataldo, 1981), therefore, there could be a relationship between grains roundness degree and beaches exposure to dominant winds. Sand grains round more efficiently under gentler wave action of the eastern side beaches whereas the more angular grains of the north-western beaches, eroded from the nearby cliffs with null or quite minimal reworking, produce angular and sub-angular grains.

Mean roundness data of Aeolian islands beaches sand have allowed to delineate a grain type roundness ranking among polymineralic and monomineralic grains. Volcanic polimineralic grains with microlitic texture (Lvmi) are always more rounded then lathwork (Lvl), vitric (Lvv) and felsitic (Lvf) textures. Among monomineralic grains, olivine and opaque minerals are the most rounded grains in all samples, including the zero order crater sand sample (e.g., Ingersoll, 1990), followed by plagioclase and pyroxene grains which have often similar roundness trend. Rounding processes of the Aeolian beaches sand are thought to result from the short transit from stream to beach environment and to shoreline wave reworking, even if, in some cases, an higher roundness degree, of some detrital species, could be also directly inherited from the crystal habit of some phenocrystals within the groundmass of the volcanic source rock lithotypes (Morrone, 2018).

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# From the Bourbon reclamation to the present landscape structure of the Volturno River coastal plain (northern Campania)

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Keywords: lan reclamatio, coastal erosion, landscape changes.

The coastal deltaic environments represent mobile geomorphic systems highly sensitive to any type of environmental change, especially those deriving from human activities that influence the landscape structure and, consequently, the ecological processes. Most of the world's coastal wetlands are located in the delta and host natural ecosystems of great ecological and economic value. Until the beginning of the last century, most coastal areas escaped human impacts as they were sites of marshes and ponds with a high incidence of malaria. In recent decades, land reclamation and the development of tourism industries, together with rising sea levels, have exposed these areas to multiple and complex disturbance agents. The changes induced by remediation have also significantly influenced the landscape on different time and scales, and above all the hydrographic system that supplies sediments to the delta plains and beaches, resulting in accelerated coastal erosion, impoverishment of the coastal environment and degradation of habitats.

The present study focused on morphological, hydraulic and land use changes that have occurred over the last 150 years in the northern Campania plain, along the eastern Tyrrhenian Sea. The analysis of historical cartography, collected, digitized and analyzed in the GIS environment, has allowed us to obtain: (1) a qualitative reconstruction of landscape changes over the last 150 years; (2) a reconstruction of land reclamation works; (3) the quantification of the resulting changes in land use and morphological configuration over the last 100 years.

Since the reclamation works, which began in the 16th century, this area recorded rapid economic development and growth in urbanization, increased above all in the last 100 years. The analysis of the landscape allowed the evaluation and quantification of the main land use dynamics, highlighting the relationships between land reclamation, urbanization growth and land use changes.

The main composition of the landscape underwent important changes until the beginning of 1900, when the reclamation works completed the channeling of most secondary courses of the coastal plain. This favored the development of agriculture and farming which were the main drivers of changes in the landscape structure. The fragmentation and complexity of the landscape increased between the 1960s and 1990s. Since the 1970s the built-up areas expanded at an accelerated rate along the coastal plain, at the expense of the beach-dune system, and along the river's course. The negative sedimentary balance resulting from the reclamation works on the river courses, together with the interventions along the Volturno river basin, resulted in an accelerated and severe coastal erosion. The overgrowth of urban areas towards the sea, combined with the intensification of agricultural and tourism activities, has led over time to the loss of high quality ecosystems such as the wet coastal environment, the retrodunal lacustrine area and, in most cases, also the beach-dune system.

The integration of landscape analysis and historical information highlights the importance of an interdisciplinary approach to land management and provides important indications for environmental requalification.

# **Session S7**

# From analogue to digital geological mapping: opportunities and risks in the use of new tools

Conveners AND CHAIRPERSONS Mauro Agate (Università di Palermo) Michele Zucali (Università di Milano) Chiara D'Ambrogi (ISPRA, Roma)

#### Structural mapping of Italian Seas: an integrated view of different geological events

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Keywords: mapping, Italian seas, EMODnet.

Since 2012 an open working group, coordinated by ISPRA-SGI, involving researchers from various universities and research institutes, has been discussing the contents and representation of a "Structural map of Italian seas."

The first step was to identify, classify and reorganize existing data, to agree on the minimum descriptive requirements needed to define meaningful structural elements, to convey all of the available structural data and to elaborate a reasoned GIS representation of the relevant tectonic elements.

Data represented in the last published version of national structural map (Bigi et al., 1990-92) have been updated and implemented by data and results obtained in the frame of the ongoing Italian National Geological Mapping Project (CARG), as well as by additional data collected by different national research institutions within other projects. They have not yet been reported in regional synthesis papers.

Since 2009 the European Union has created a coordinated and harmonized web GIS service regarding geological knowledge of submerged areas by means of the EMODNet - Geology Project (<u>http://www.emodnet-geology.eu/emodnet/srv/eng/home</u>). Within the Work Package dedicated to "Geological events and probabilities" (led by the Geological Survey of Italy-ISPRA) procedures to collect geological data concerning earthquakes, volcanoes and submarine slides have been identified.

The comparison of all available tectonic lineaments with the outcomes elaborated for EMODnet-Geology has led to the identification of the structural elements as basic components for an updated and more complete structural model for the Italian submerged areas, in agreement with the model established on land.

Regional scale structural domains ("crustal units") have been defined according to a geodynamic approach, also based on the characteristics of volcanic seamounts, grouped into districts identified on the basis of chemical composition, age and geographical location. Structural elements, classified according to EMODNet terminology (INSPIRE compliant), will be mapped starting from this representation.

The map is intended to provide a scientific useful tool for either basic or applied research, as well as for scientific learning, since it represents the "state of the art" at the end of a decades data collection period and allows at the same time both a synthetic overview of the geological structure of large areas, and to grasp the most significant regional structures of a given sector.

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# Digital mapping of submerged areas: from the planning to the development of the final products

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Keywords: Digital mapping, European Project, Database.

EMODnet Geology is a European Project which promotes the collection and harmonization of marine geological data in European Seas. All these data are subdivided into Work Packages (WP), referring to seafloor sediments grainsize, sedimentation rates, Quaternary and pre-Quaternary geology, coastal behaviour, geological events and mineral resources.

The Italian geological mapping has contributed constructively to the realization of geological datasets, harmonized at European level, in which all the geological knowledge of the various European countries have been merged.

The Project, at the end of its second phase, has made available harmonized digital maps at 1:250,000 scale, with additions to the scale 1: 1,000,000 where more detailed data were not available. The third ongoing phase is aimed at obtaining products at least at the scale of 1: 100,000 or more detailed.

The Geological Survey of Italy - ISPRA leads WP6 "Geological events and probabilities" with the aim to identify and map significant geological events occurring in European Seas that include: submarine landslides, earthquakes, volcanic centers, tectonics, tsunamis and fluid emissions of non-volcanic origin.

The sources of data are all pre-existing data in literature which also include cartography, databases, national and European projects. All these data were processed for the final purpose of producing digital cartography freely distributed as WMS services on the EMODnet Geology Portal.

The realization of the digital cartography of WP6 has been divided into several phases:

- elaboration of Guidelines and preparation of the Table of Content with technical specifications on how to supply GIS layers; during this step we have identified the parameters that should be used to characterize events and any additional relevant information. Particular attention has been devoted to the definition of the Attribute table in order to achieve the best degree of harmonization and standardization according to the European INSPIRE Directive
- systematic collection of basic data, visualization and identification of any areas without data;
- generalization. The maps are generalized on a scale of destination. Datasets consist of shapefiles representing each event at 1:250,000 scale in Emodnet Geology2 and at 1:100,000 scale in Emodnet Geology3.
- harmonization of data according to specifications;
- data processing, compilation and structuring of shapefiles in European-wide layers;
- update, correction and implementation of files after review by partners.

One of the objectives pursued was the interoperability of data, in order to provide more complete, correct and reliable information and facilitate the exchange and reuse of data even among non-homogeneous systems. Besides combining these harmonized and standardized datasets, it might be possible to develop additional thematic maps that could support further research, as well as the planning and management of submerged areas.

#### Web mapping-based solution for integrated management of geological and geophysical data

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Keywords: web mapping, Geographic Information Systems, Geological and Geophysical data.

The Structural Geology and Geophysics group (GSG) of the Department of Physics and Geology of the University of Perugia has gathered a large amount of geological and geophysical data during years of research and projects. These data, acquired from both digital and analogue sources, include geological maps, seismic reflection profiles, deep boreholes and gravimetric measures providing precious information about the surface and subsurface geology of Central Italy. In order to organize and to exploit this information, we have developed an open-source, web mapping-based application for dynamic access, query and visualization of geological and geophysical data along with several GIS capabilities..

The main aim of this work is twofold: on one hand, the compilation of all the data collected by the GSG group for the creation of an updated database. On the other hand, providing a centralized system with webbased access reachable to the researcher as a platform for fast data recovery. The tasks performed during the phases of data compilation, conditioning and setup were conducted using mainly the Geographic Information System (GIS) QGIS v2.18 desktop, among other modelling and geoprocessing packages (GDAL, SAGA, TileMill). Then, GIS data were imported to the World Wide Web by using Leaflet JavaScript library for the generation of interactive maps..

The web application contains several navigation and interaction tools (zoom, pan, full-extent, control switching layers, sidebar object-filtering, areas and distances measurement) visualization tools (index map, metric scale, mouse position coordinates) and query tools (access to attribute-tabular information and associated documentation with a new window or popup, search by place, by coordinate and by object). Other functionalities such as fast data downloading and cartographic layout are also available. All the data have been converted into standard formats and have been referenced to the main Coordinate Reference Systems. In this way, their interoperability is allowed when operating within other software and systems, such as those intended for geological modeling..

The results obtained from this work show the successful combination of QGIS for desktop mapping and Leaflet JS for web mapping to provide an integrated framework of multidisciplinary datasets. This digital tool will favor the exploitation of this information contributing to the research activities of the community and helping in adopting a multidisciplinary research approach.

# Filling the gap between the GIGAMAP and the GNS maps in Victoria Land, Antarctica: geological mapping in the Convoy Range

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Keywords: geological mapping, Convoy Range, Victoria Land.

In the austral summer 2017/18, in the framework of the 33rd ItaliAntatyide Expedition, a three person team performed geological and geological-glacial field mapping in the Convoy Range (Victoria Land, Antarctica), at the scale 1/250'000. Activity was heli-supported, starting from the Italian base in Terra Nova Bay (Mario Zucchelli Station), and interested the Convoy Range and the Franklin Island quadrangles of the USGS 1/250'000 Reconnaissance Series. The activity had two principal targets:

- to fill the gap existing between the area covered by the GIGAMAP programme (Pertusati et al., 2016) to the north and the geological maps by GNS Science (New Zealand) to the south (Gunn & Warren, 1962; Pocknall et al., 1994; Cox et al., 2012), by mapping the area comprised between 76° and 76°30'S and between 159° and 163° E;
- to collect new data (stratigraphic, structural, sedimentological and petrographic data) to better characterize the lithotectonic units cropping out in the investigated area.

In more detail, in Antarctica the activity included geological and geological-glacial field mapping, photogeological analyses, structural observations and rock sampling. In this area, the dolerite and basalt of the the Ferrar Group and the sandstone of the Beacon Supergroup (i.e. the rocks of the Gondwanian sequence) are prevalent. Granites and granodiorites of the Granite Harbour Igneous Complex constitute the crystalline basement underlying the Gondwanian sequence; such basement occurs only in the sector that is close to the Ross Sea coast. Minor enclaves of Wilson Terrane gneiss are hosted in the Granite Harbour granitoid. During the mapping activity, we collected rock samples (more than 120) for subsequent laboratory analyses and also gathered attitude measurements of bedding, faults and fractures. For the glacial geological mapping, we collected rock samples to perform Surface Exposure Dating, by analyses on selected cosmogenic isotope.

On return from Antarctica, the activity comprised digitisation of the new cartographic data and their integration in the digital dataset of the Geomap Action Group; elaboration of structural data; microstructural analyses and minero-petrographic analyses of rocks and glacial deposits.

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# Multiscale and Multidisciplinary approach to support the remediation strategy of the Decimomannu military Air Base

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Keywords: Geodatabase, Hydrogeophysical Model, 3D.

The presented contribution focuses on the essential role of the proper collection, storage, representation and integration of geo-thematic data from different sources in defining reliable remediation strategies for contaminated sites. An illustrative case history is here presented concerning the Military Airport of Decimomannu (CA), affected by various aviation fuel (JP8) spills in 2007 (40000 l), in 2009 (5000 l) and in 2010 (5000 l). The creation of a "4D" geographical database (which also considers the timing factor) contemplates the integrated management, representation and analysis of different data (geological, hydrogeological, hydrogeochemical and geophysical). The 3D Hydrogeophysical model represents the decision support system that allows to increase the effectiveness of the analysis as it provides support to all those who must make strategic decisions. The main function of a 3D georeferenced model is to extract in a short time and in a versatile way the information useful for decision-making processes, coming from a significant amount of data. The representation of the geological structure through a 3D model facilitates its understanding and depicts the hydrogeological setting. Geophysical prospecting strengthens the stratigraphic model and increases the degree of detail in terms of spatial resolution. The ERT data, acquired along a line, bring to data spatialization and geological model refinement. The piezometric surveys and the analytical measurements permit to reconstruct the groundwater circulation and the groundwater contamination status evolution. Pumping tests and the slug tests provide the hydraulic parameters of the aquifer. The analysis of water quality status evolution highlights the presence of hydrocarbons in residual phase. LIF-CPT surveys delimit the presence of residual phase along a vertical profile with high resolution and provide a high resolution "lithotechnical" log. The complete multidisciplinary and multitemporal characterization allows to identify the critical areas (where most of the contaminants are present) and supports the choice, the sizing and the configuration of the remediation technology to be implemented. To test the operation of remediation intervention, it was scheduled a first intervention (at detailed scale) in a "Pilot Site", in order to obtain technical and operational information necessary for the optimization of the latter on a wider scale. The innovative strategy consists in the injection of reagents in the subsoil that can reduce contaminant concentrations in soil and groundwater through the combined action of (i) Desorption of contaminants from the solid soil matrix (where they are adsorbed) to the liquid matrix through the use of an inorganic chemical reagent (PetroCleanze®); (ii) Recovery of dissolved contaminants by subsequent pumping.

# From traditional fieldbook to tablet and drone-aided mapping techniques: an application to the coseismic ruptures survey following the 2016 central Italy earthquakes

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Keywords: Earthquakes, new techniques for field surveying, tablet and drone.

In the last decades, the traditional techniques of geological mapping have been integrated by the use of several types of instruments as tablet, with dedicated softwares, and drones (Unmanned Aerial Vehicles -UAVs).

The latter have become widely available in structural geology and, being a remote sensing technique, they offers multiple advantages compared to the traditional fieldwork. They enable the reconstruction of three dimensional models of inaccessible outcrops, and to explore in detail areas which, during an intense seismic activity, may be affected by rock falls (cliffs or outcrops at the foot of prominent fault scarp).

Here we report on the fieldwork during which the above mentioned technologies were an useful tools to reduce sensibly the working time and to collect massive datasets. During the 2016 Central Italy seismic sequence after the Mw 6.0 (August, 24) and Mw 6.5 (October, 30) earthquakes, we performed a detailed survey of the cosesimic features throug the digital field mapping application "FieldMove", developed by Midland Valley (www.mve.com). We mapped over 3800 survey sites along the Vettore-Bove fault over a total lenght of about 30 kilometers. We collected different types of data, such as: rock type, bedding, striated/unstriated fault planes and ground fractures, associate displacement, in some cased assessing both heave and throw.

Part of our dataset collected after the October 30 mainshock, was shared with the Open Emergeo Working group and is available in Civico et al 2018 and Villani et al. 2018.

Locally, the digital mapping was integrated by thedata acquired through UAVs that allowed to collect further 800 data along the 100 m-long "Colli Alti e Bassi" fault trace, one of the subsidiary structures reactivated during the Mw 6.5 earthquake. Our results highlight a great speed of acquisition combined with the good quality of the collected data, as shown by the comparison with some traditionally surveyed sample sites, used as calibration points. Some difficulties still occur during the post-processing phase, that is very hard to manage due to the huge amounts of acquired data. In the study case, these problems were overcome by using specific photogrammetry software for professional drone-based mapping and other software like ArcView GIS - Move 2018, and above all using very high performing hardwares.

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### The INSPIRE directive and geological data: how far have we got?

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Keywords: INSPIRE, Spatial Data Infrastructure (SDI), RNDT.

The geological data repository is composed by more than 10 geodatabase, great part of them available at the Geological Survey of Italy Portal (<u>http://portalesgi.isprambiente.it</u>)shared in standard formats. For each dataset have been compiled the metadata file and the WMS (Web Map Services), WFS (Web Features Services) and WCS (Web Coverage Services) services have been published, in agreement with the INSPIRE Directive and its Technical Guidelines. All of metadata are archived in a catalogue exposed as CSW (Catalog Service for the Web) 2.0.2. In this context, AgID (L'Agenzia per l'Italia Digitale) supports the Administrations and contributes to the implementation process of the technical rules in particular for the purposes of interoperability. The article 59 of the Code of the Digital Administration (CAD) has founded the National Repertoire of the Territorial Data (RNDT) that disciplined the adoption of the technical rules for the training, the documentation, exchange and the re-use of the spatial data held by the public administrations. With the setting up of the National Committee for Spatial and Environmental Information (CNITA - art. 11 of Legislative Decree 32/2010 decree transposing the INSPIRE Directive), that process may be carried out within the technical sections identified within the scope of that Committee. The Geological Survey of Italy will participate to the working group of the CNITA that will concern: cooperation, metadata, data specification, network services, data and services sharing, monitoring and reporting.

### 3D modelling of fabric domains in the eclogitised continental crust of the Mt. Mucrone area, Sesia-Lanzo Zone, Western Alps

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Keywords: Fabric evolution, Metamorphic trasformation progress, Multiscale analysis.

3D modelling based on multiscale correlation of superposed structural and metamorphic imprints, can be an excellent tool for evaluating rock volumes that recorded different degree of fabric evolution consequent to strain partitioning characterising succesive tectono-metamorphic stage in the metamorphic basements. A quantitative 3D representation of volumes with homogeneous degree of fabric evolution (DFE) is inferred for the HP-LT metamorphic rocks of Mt. Mucrone area that consist of polydeformed continental rock during Alpine subduction (Zucali et al., 2002; Delleani et al., 2013). Alpine heterogeneous deformation allowed the fabric preservation in pre-Alpine magmatic and HT metamorphic relicts from widely eclogitised metagranitoids and metapelites, respectively. Multiscale structural analysis reveals seven groups of superposed structures developed under eclogite facies (D1 to D3) and successively under blueschist facies (D4) during subduction, to greenschist facies (D5 to D7) throughout the continental collision. D2 structures dominate and mainly consist of isoclinal folds associated with a pervasive foliation.

Multiscale structural and petrologic data are used to synthesise syn-D2 structural and metamorphic heterogeneities on maps of fabric evolution and metamorphic reaction progress. The definition of domains characterised by different degrees of fabric evolution is based on the estimation of grain-scale reorganization during D2 (planar fabric: 0-20%; 21-60%; 61-100%). The individuation of domains with different degrees of reaction progress (DRP) is based on the modal amount of syn-D2 minerals (0-20%; 21-60%; and 61-100%). These domains are georeferenced and stored in a geo-database set on a geographic information system (GIS). The fabric domain map linked to digital elevation model, eight interpretative cross-sections, and orientation data of the structural elements are used to quantify volumes with Geomodeller software. The model allows defining the size, shape, and spatial relationships of rock volumes showing homogeneous DFE. The results indicate that domains of high DFE covered ca. 85% of the modelled volume and their relationships with DRP show that they generally are characterized by the highest DFE. The results also demonstrated that this approach is a powerful tool to unravel the different relationships between DFE and DRP during superposed tectono-metamorphic stages, characterized by contrasted PT conditions.

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# From geological field survey and biostratigraphic analysis to 3D geological modelling: some of the ongoing activities at Servizio Geologico d'Italia

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Keywords: geological field survey, biostratigraphy, geological mapping.

Geological field survey is one of the most traditional and typical activity of the Geological Survey Organizations around the world.

The Servizio Geologico d'Italia (SGI) is not an exception; field geologists and biostratigraphers work together to collect base data that are used to: i) produce geological maps, ii) develop stratigraphic studies, iii) support emergency inspections and seismic microzonation studies, and iv) give input data for 3D geological models production.

In the last years several geological sheets at 1:50,000 scale have been realized directly by SGI field geologists and biostratigraphers: F. 280 Fossombrone (2016), F. 413 Borgo Grappa (2016), F. 345 Viterbo, F. 347 Rieti, F. 386 Fiumicino, F. 348 Antrodoco. They cover a wide range of stratigraphic and structural contexts from Apennines fold and thrust belt to coastal areas and volcanic regions.

More recently SGI has received funds from Regione Lazio for the completion of the F. 337 Norcia (in collaboration with CNR IGAG), that covers the core of the area struck by the 2016-2017 Central Italy seismic sequence.

The F. 337 Norcia benefits from the knowledge on similar stratigraphic and structural setting, studied and mapped in detail in the contiguous F. 348 Antrodoco, and from a continuous field activity, more than one year long, supporting National Department of Civil Protection (e.g. geological and hydraulical compatibility evaluation of location for temporary houses and schools, and prompt evaluation of slope stability for road network safety conditions) and Centro per la Microzonazione Sismica (i.e. geological support to professional geologists in charge for level 3 seismic microzonation).

This area of the Central Apennines is interested also by SGI 3D modelling activities in the framework of the ongoing RETRACE-3D Project (with INGV, CNR and DPC), where surface data are integrated with subsurface ones to obtain a 3D crustal model.

Definitely the Norcia geological sheet is paradigmatic of the role and importance of collection of basic geologic data, derived from field survey and analyses, to produce information for further applicative purposes.

Furthermore a wide range of tasks are carried out for an Agreement with Regione Abruzzo: new detailed field survey and mapping in the foothill areas surrounding the Majella; harmonization of existing geological maps toward the definition of a continuum at regional scale; support to the level 1 seismic microzonazion studies.

The SGI geologists, combining litho- and bio-stratigraphic analyses and benefitting from the integration of traditional and modern tools for data collection, produce a geological knowledge zooming from regional to local scale, from surface to subsurface, from geological mapping to 3D modelling, both for scientific and applicative purposes.

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#### **3D** modelling and printing geology of Monte Fumaiolo: back to analog representation

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Keywords: 3D geological model, 3D printing, Epiligurian succession, Northern Apennines.

Monte Fumaiolo can be interpreted as an hybrid carbonate-terrigeneous platform of the Miocene Epiligurian Succession as it was deposited and transported on top of the Ligurian Nappe of the Northern Apennines (Amorosi, 1992; Conti et al., 2015; Fontana et al., 2015).

This work propose an original 3D geological model of the remains of this platform after extensive landslides and erosion, derived from GIS digitalization of the detailed maps of the project "Geological Map of Emilia-Romagna Region at the scale of 1:10,000" (De Donatis, 1995 a-b).

Following some site inspection and checking the interpreted stratigraphic boundaries and faults, the work has been focused on defining the shapes and volumes of each mapped unit.

Some simplification was necessary when Quaternary covers and landforms masked the substratum geology. Moreover the heteropic transitions of the sedimentary units and tectonics enhance the complexity of the boundaries interpretation in three dimensions.

Nevertheless, using Move software, we could arrange a tentative model taking in account also the fault deformation. Blender, an open source software designed for cartoons animation mainly, enabled to make a first 3D printing experience producing a sort of three dimensions jigsaw puzzle. This almost self-explaining analog representation can be also useful for improving geology acquaintance for non-geologists.

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#### **Open source in field geology: a QGIS-mate Android compass**

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Keywords: Open-Source code, Geopackage, Digital Geological Compass.

BeeDip is a digital geological compass developed by students and researchers of Urbino University under open source license (GPL) dedicated to the open source QGIS software. The app can be installed in any Android smartphone. Previous apps are able to measure different kind of geological data, but all of them keep a "closed" code (Weng and Grigsby, 2012; Lee et al., 2013).

The connection with QGIS is guaranteed by an homonymous plug-in (Phyton developed) which enable the export/import of data and maps from and to the GIS project. The used file format is Geopackage (OGC, 2017), under open source MIT license. This allows to import in the app any georeferenced and tiled geotiff map file, enabling the off-line and custom map visualisation with appropriate symbols and labels. Also the data transfer from the app to QGIS has been facilitated.

The digital compass can record surface and line measurements, adding other complementary data/metadata and organising them by projects.

Tests and comparisons have been performed to assess the validity of this system in the lab and in the field concluding that the data acquisition is fast and simple, but devices can be calibrated and the accuracy depends mainly on built-in sensors (Novalowa and Pavlis, 2017). The app and the plug-in are open to any contribution of developers and users.

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# Lithological and structural characterization of the range front of the Monte Gorzano fault (Laga-Campotosto fault system): understanding the 2016-2017 earthquake ground effects

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Keywords: coseismic ground deformation, ground failure, field mapping.

The Quaternary Laga-Campotosto fault system runs from SE to NW beneath the Campotosto and Amatrice villages (Central Italy). Although the 2016-2017 earthquakes generated intensity up to XI MCS in Amatrice and nearby villages, very little evidence of earthquake ground effects has been recognized along the active Laga-Campotosto range front. With the aim to define possible ground deformation and ground failure related to the continuing seismic sequence, and distinguish modern from past deformation style that characterizes the Campotosto and Amatrice areas, a multidisciplinary study has been conducted. Here we present the preliminary result of ongoing investigations based on a stratigraphic, sedimentological and structural approach.

In the Campotosto sector, the main capable fault plane generally runs hidden by recent colluvial deposits, Late Pleistocene to Holocene peat of the Campotosto basin, and the hydroelectric basin (the second largest in Europe) created in 1939-40. In particular, the Rio Fucino dam is located on the tectonic threshold of the basin, where the Late Quaternary fault displacement blocked the Rio Fucino drainage flowing toward the Adriatic Sea. Scattered outcrops document that the fault crosscut the arenaceous member of the Laga Formation, dipping SW-ward with high angles (60°-80°). Nor ground or bedrock deformations from the last earthquake sequence have been observed, although clear paleoseismic displacement and tectonic structures related to past surface faulting events (e.g. sandy gouges, rotated blocks) have been observed in the Laga Fm. sandstones.

Near Amatrice, the pelitic and arenaceous members of the Laga Fm. are in contact with the underlain Marne con Cerrogna Fm. along the principal NW trending fault plane, buried under the colluvial detritus. Secondary planes, SW high-angled (70°-80°) dipping, are identified crosscutting the sedimentary sequence east of the main plane. Potential coseismic and paleoseismic deformation (e.g., road displacement, aligned gullies) have been identified both in the colluvial deposits and at the boundary between bedrock and slope deposits. Other mapped structural features, essentially related to paleo-tectonic stages, are a NE trending strike-slip fault and open folds in the Marne con Cerrogna Fm.

Coupling all these results together will lead to a better understanding of the areal response to the latter earthquake events, and the improvement of the regional seismic hazard assessment.

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# Digital tools for improving field geological mapping. A case study from the Regional Reserve of Montalbano Jonico Badlands (Basilicata, Southern Italy)

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Keywords: Tablet PC, Lower-Middle Pleistocene transition, badlands.

In recent years, the evolution of the geological mapping discipline, has undoubtedly benefited from technological progress, and the use in the field and in the laboratory of new important IT tools (e.g. Whitmeyer et al., 2010). The traditional field equipment was partially accompanied and/or replaced by ruggedized portable personal computer with integrated GPS receivers and GIS software devoted to record in greater detail a wide spectrum of geological data, to facilitate the correct location of the geologic features on the map, to draw a geo-referenced digital geological map in the field and to save data in a great variety of file format.

As a case study we present a geologic map, 1:10.000 scale, based on digital field data implemented in the Regional Reserve of Montalbano Jonico Badlands (MT). The Reserve is located on the western border of the Southern Apennines Quaternary foredeep (Bradanic Foredeep). The main geological peculiarity of this area is represented by the excellent exposure of a marine reference section, straddling the Lower-Middle Pleistocene transition (e.g. Marino et al., 2015, *cum bibl.*). The geological framework of this area is relatively simple: the substratum is represented by the argille subappennine (Azzaroli et al. 1968): several hundred m thick of muds and muddy silts, with nine thin volcaniclastic intercalations, having a monocline setting gently dipping toward east and an unconformably cover represented by Middle Pleistocene marine terraces (e.g. Vezzani, 1967) and Upper Pleistocene - Holocene alluvial deposits. Furthermore, the clayey hillslopes of the Reserve show erosional landforms giving rise to a stunning badland landscape. The goal of the map was to promote the stratigraphic and morphologic scientific peculiarity of Montalbano Badlands, well known and appreciated by geological specialists, to the broadest public and geo-tourists for educational purpose and joyride. Moreover, the map produced by a traditional geological survey supported by the use of tablet PC, a mobile GIS application and QGIS software allowed us to collect, storage, and draw up further geo-referenced geological data of potential scientific interest to be valued in the near future.

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### The new Portal of Geological Survey of Italy (ISPRA): improvement of use of information

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Keywords: geoportal, interoperability, geological data.

Since more than 140 years, the Geological Survey of Italy is in charge to collect, manage and disseminate geological data of Italy, with specific concern to cartography, in agreement with Law n. 68&1960 that indicated it as the official National Cartographic Body. The Portal available at <u>http://portalesgi.isprambiente.it/</u> is the gate to access to all the available geological data of interest for the italian peninsula. It has been realized with the aim to share, integrate and disseminate the huge amount of data collected in the datasets owned by the Geological Survey of Italy. The Portal was developed following the recommendations of AGID (Guidelines for the design of digital services of the Public Administration), using a starting kit available in 2017. In order to 'strengthen' the system, the open source CMS Drupal platform 8.53 was adopted for the management of contents on the web. Most important is the component of metadata management and services realized through the Esri Geoportal, now in version 1.2.7. The ten-year collaboration with ESRI Italy has made it possible to update the old catalogue and integrate it into the new Portal. The Geological Survey of Italy has improved over 40 of database and data sets, including basic and thematic geology, natural risk, geophysics, wells, 3D modeling, geo-resources, geosites, land use, land cover, etc. A set of tools for viewing data is available: the first map viewer has been customized starting from an open-source framework web with the ability to navigate in 3D, TerriaJS. In addition to the basic standard tools, it is possible add data in the json, csv, kml, kmz, geojson, etc. format. The identifier takes place on the element of interest and downloads the attributes. The second 2D viewer, realized by ESRI Italy, allows the user to navigate directly in content, starting from the metadata catalogue. This viewer allows consultation of several catalogues: the user can add other dataset layers (shp.zip), wms layers e.g. coming from ArcGis online or from other repositories. There are available several thematic viewers created to make more accessible the data for national and international projects, among which ITHACA viewer, TSUNAMI map viewer, Central Italy Earthquake, August-October 2016, viewer, etc.

# Structural mapping of UHP serpentinites at Créton, upper Valtournenche valley, Zermatt-Saas Zone

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Keywords: form surface map, petro-structural analysis, Alpine subduction.

Detailed field mapping (1:20 scale) and multiscale petro-structural analysis were applied to a portion of the Zermatt-Saas Zone in upper Valtournanche (Western Italian Alps). The analysis is focused to infer, by the superposed fabrics and structures and the associated mineral assemblages, the relative chronology of successive tectonic stages in polydeformed serpentinites involved in a subduction system. The results are synthesised into a map with foliation trajectories, transposed lithostratigraphy and syn-kinematic mineral assemblages of keyoutcrops at Créton barns. Serpentinites comprise magnetite layers and rare, dm-thick, diopsidite layers and lenses. Moreover, veins and aggregates of Ti-chondrodite and Ti-clinohumite, layers and lenses of dunites, veinlets of olivine, and layers of dark pyroxenite are embedded in serpentinites. All these rocks record three groups of syn-metamorphic ductile structures: D1 consists of rare fold hinges and a relic S1 foliation, preserved in S2 lithons; D2 comprises isoclinal folds and a very pervasive foliation (S2), which is the dominant fabric at the regional scale (Zanoni et al., 2012; 2016); D3 includes a crenulation, shear zones and open folds. The detailed structural fieldwork, supported by microstructural analysis, allowed to correlate these outcrops with the regional setting described in previous works (Rebay et al., 2012; Zanoni et al., 2012) and to identify pre-D2 structural, mineralogical, and textural relicts that are preserved regardless the strong transposition produced during the development of S2 HP-UHP foliation (Zanoni et al., 2016 and refs therein) which was recently dated at ~65 Ma (Rebay et al., 2018). The occurrence of Ti-chondrodite in pre-D2 Alpine assemblages suggests that suck rocks re-equilibrated at UHP conditions (P= 2.8-3.5 GPa, T= 600-670 °C; Luoni et al., 2018), similar to those of the adjacent Cignana Unit, suggesting a new Alpine tectonic setting for the ZSZ.

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### Integration of GIS and AutoCAD informative systems for the execution of the "Gronda di Genova" highway tunnel

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Keywords: "Gronda di Genova" highway tunnel, Geological mapping, GIS.

Geological maps/geodatabase are tools able to represent several geological information, such as the different types of rocks and their spatial relations, as well as many other information of chemical-environmental nature (i.e asbestos content) or geotechnics (i.e. landslides).

These information provide the constraints on which the reference geological model is built.

Geological maps are now realized using computer technologies (GIS systems) that allows the acquisition, recording, analysis, visualization and restitution of georeferenced data.

The integration of multiple geological and environmental themes can be an important issue to meet the needs of the end user.

The use of GIS technologies is increasing not only for the land management (e.g. in environmental agencies) or among scientists, but also in industry, namely in the design of major infrastructures placed in critical environmental settings.

In the study case, a geoengineering project (the highway by-pass tunnel known as "Gronda di Genova") gave us the chance to merge into one single informative system multiple information acquired for both technical and environmental protection purposes.

The complex geological setting interested by the infrastructure (very different geological units, presence of asbestos-bearing rocks, major fault zones, a lot of landslides etc...) required an integrated approach to represent (at different scales, from AutoCAD layout to Web\_GIS application) the geo-environmental issues, in order to allow an effective understanding of the critic impact of the tunnel on the territory.

In order to achieve the above described goals, the GIS geodatabase has been designed on the base of a robust conceptual models and compiled with shared vocabularies for the geo-environmental sciences. This in the order to allow interrogation of database in accordance with shared (local, national or international) descriptive standards.

Example applications will be reported in this contribution, referring to several study cases taken from the Gronda di Genova surface and subsurface database, consisting of thousands of field observation, hundreds of drill logs, several geophysical sections and a great quantity of minero-chemical analyses on rocks and sediments.

# 3D mapping of geological structures: from promise to the reality 3D mapping of geological structures: from promise to the reality

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Keywords: geological map, digital survey, 3D outcrops.

In the last years the geological field survey benefits of the digital technology reaching a mature procedure, that improve its efficiency. The available technology permits to acquire easily spatial data, changing the methods of representing and synthesize geological knowledge, shifting from a static to dynamics representation, continuous updatable, using different methodological approaches and sources of data at variable scales. This is the main challenge in order to represent the real tridimensional geological structures, making the 2D map inadequate to represent the potential available information. In the digital millennium, the main contribute to the geological field survey derive from the GNSS (global navigation satellite system) geolocalization, probably the best geological tool after the compass. In the last decade, 3D virtual outcrops derived from the LIDAR (Light Detection and Ranging) technology, which is limited by the cost and by instrumentation required. The main step to the 3D world derive from the digital photography, which is not only recorded outcrop images at no practically cost but because it contains a huge amount of numerical information. These numerical data can be easily extract with the aid of the computer vision technology. A new generation of algorithms like "Structure from Motion" or SfM developed in few software, permits to obtain 3D spatial geolocalizated clouds of data. Starting from few digital photos a 3D virtual outcrops can be built, making photogrammetry available to a growing number of Earth scientists. Most recently the flying platform systems ready-to-use, like small Unmanned Aerial Vehicles or UAVs, able to carry different type of payload including sensors and cameras, represent the final loop of this digital revolution. These UAVs use a flight control unit (FCU) able to process autonomous and remote navigations commands from the pilot, which get avionic data from one or more inertial measurement unit (IMU), magnetic compass and one or more GNSS receivers also with RTK (real time kinematic) capability. The combination with low altitude photos, both zenithal than oblique, permits to obtain easily georeferenced 3D point clouds with centimeters accuracy. Topography or DSM maps are the direct products, but the possibility to analyze spatial geological structures especially in hazardous or inaccessible areas, represent actually one of the important application. There is the possibility to build real accuracy 3D models where the geological features can be analyzed from many viewpoints, repeatedly and practically at no cost. This allowing rapid evaluation of the geometry of the structures with the possibility of further analyze and interpreted from geologists with different experiences. Starting from few examples, in the different structural contest from simple outcrops to complex coseismic ruptures patterns, the efficiency, precision and limits of these technologies and methodologies are discussed.

# Drafting the provincial road safety plan as an opportunity to develop a platform for the geological risk assessment in the territory of South Sardinia Province - Italy

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Keywords: Mapping, Risk management.

Within the road safety plan, the Province of Southern Sardinia has implemented a particular intervention concerning the preparation of an interactive SIT platform as a tool able to support decisions for the planning of interventions to be foreseen along the patrimony roads.

Among the main functions envisaged is the one concerning the verification and updating of the risk mapping on the parameters concerning the geological and hydrogeological risk, paying particular attention to the mapping variation in the updates concerning the cartography data of the Autonomous Region of Sardinia on the Asset Plan Hydrogeological, the Floating Plan of the River Bands, the Flood Risk Management Plan. These data will be constantly implemented and updated, and then visible by the officials of the technical service, in association with those who will populate the database regarding all the interventions that will be carried out, the themed reports forwarded by the police and other bodies responsible for the protection of public safety. The structure of the GIS platform, in advanced elaboration, will be a powerful tool to support the planning of the interventions on the geological and hydraulic structure of the territory of competence, for the planning to be carried out on an annual and multi-year basis by the Province of South Sardinia in the short, medium and long term. Additional data to support the GIS platform, already acquired at the scale of greater detail, will be those relating to the Roads Cadastre: the latter, through the use of a Web interface, will allow you to give a first sizing and calculation of the interventions, pointely and extensively, from put in place for the protection of the population, even under civil protection, thanks to the provision of an updated historical database and then with the possibility of evaluating the mapping of what has already been done previously in the various years. The interfacing with the geological multiprecision database of the region will lead to assessing the geological parameters insisting on the area studied in order to detect the geomorphological and geotechnical criticalities that characterize the zone of study and in this sense zoning the various parts of the provincial territory.

The SIT platform is based on a particularly userfriendly web interface, structured in hosting on operating system (Linux platform) and management software (GIS, Geoserver, etc.) completely opensource, interchangeable with each other and in any case easily updated and implemented by any operator sector. In beta testing, a wide compatibility with the classic software platforms and with all the most used web browsers has already been verified.

The possibility of continuously implementing the detailed and extensive data collected and made available by the operators and officials of the Province, also through dedicated Apps, will be able to summarize the expenses and the programming of the interventions with objective data that many times turn out to be secondary importance at the time of the decision.

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# Deterministic vs. Stochastic interpolation methods in geochemical mapping of plutonic complexes: Automated mapping via IG-Mapper of the Squillace pluton (Serre Massif, Southern Italy)

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#### Keywords: Kriging/IDW interpolation, Python, Lithological maps.

Plutonic complexes are the result of multiple emplacements of different plutonic bodies, whose composition can be differentiated through mechanisms such as fractional crystallization, mixing or assimilation. Tectonics can further influence the final rock type distribution, largely modifying the original primary contacts.

Therefore, rock type distribution within a plutonic complex can be described as the result of the interplay of deterministic (i.e. driven by a specific gradient) and/or a stochastic (controlled by a probabilistic rule) processes.

For these reasons, we developed a new GIS-based automated package tools (IG-Mapper - Fiannacca et al., 2017) for the interpolation of geochemical parameters of plutonic rocks based on the alternative choice of a deterministic (i.e. Inverse Distance Weighted - IDW) or a stochastic (i.e. Kriging) interpolator.

IDW is based on the multivariate analysis of selected mapped variables whose influence decreases with the distance between its sampled locations. The most important parameter to consider using the IDW is the "Power", which allows checking the meaningfulness of the known points with respect to the interpolated values, based on their relative distance.

Kriging is a non-deterministic algorithm based on the calculation of an autocorrelation function among sampling points for a specifically selected parameter, which has to be considered to vary with continuity in the region of interest. Kriging is also a best linear unbiased estimator (BLUE) based on a regional variable (RV), which tends to be correlated at specific scales and decreases with the increase of the distance calculating at the same time the magnitude of the reliability of the interpolation.

IG-Mapper produces also lithological maps based on TAS (Middlemost, 1985, 1994), R1-R2 (De La Roche et al., 1980), Q-ANOR (Streckeisen and Le Maitre, 1979) and Ab-An-Or (Barker, 1979) classification diagrams.

The obtained lithological maps provide a reconstruction of the field relationships between different lithological units with an estimate of geostatistical reliability achievable through the construction of interpolation checking maps.

These last maps provide an estimate of the geostatistical interpolability for one specific parameter at a time, calculating an empirical index (Stochastic Interpolation Index), able to highlight the randomness of a specific value distribution.

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#### Metamorphic Geo-Petrology Information System (MetGeoPetIS): a new cyberinfrastructure for numerical metamorphic geology data management

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Keywords: Metamorphic Geology, Thermodynamic modeling, Earth Science automated tools.

Distribution of metamorphic rock textures within a tectono-metamorphic unit (Gosso et al., 2015) is the result of the counterbalancing interaction of deformation (controlled by rheological behavior of the more abundant mineral phase) vs. crystallization (controlled by the thermodynamic equilibria rules) processes. Deformation processes are normally more influent than recrystallization ones due to the higher strain-rate respect to the blastic recovery rate within most of the PT range of metamorphism.

The quantification of the rheological properties from field- to micro-scale, as well as the definition of the different metamorphic assemblages, stabilized during each recognizable metamorphic evolutionary stage, represents then the crucial aspect to be investigated to reach a rigorous logical scheme at the base of a metamorphic geo-petrology database.

In this view, we would like to structure for the first time a unique information system that, starting from the accurate subdivision of the metamorphic rock texture distribution in the field, permits to obtain a correct classification of the selected representative samples. These samples are used to constrain quantitatively the sequence of the PT conditions as well as the changes in the rheological behavior occurring during the superposed stages of an entire tectono-metamorphic evolutionary cycle.

After the definition of a GIS reporting the metamorphic rock-texture distribution in the field, MetGeoPetIS continues with the acquisition of high-resolution optical thin section scans used to obtain grain size distribution (GSD) and the shape preferred orientation (SPO) of mineral grains. Derived results are then integrated with the multivariate statistical image analysis of micro X-ray maps of the entire thin section to transform the GSD analysis in a mineral distribution map. The following classification of one or several microdomains per thin section, highlighted then in turn, the sequence of recognized metamorphic equilibria, can be used to a better definition of the effective bulk rocks chemistries (e.g. Ortolano et al., 2014).

The workflow continues with the calibration of previously classified X-ray maps via a multilinear regression technique (Ortolano et al., 2018) which permits to obtain: a) maps of element concentration per mineral phase (expressed in a.p.f.u); b) maps of end-members fractions visualizing potential occurrence of zoning patterns. Yielded results highlight as this new GIS-based workflow can be usefully applied to store, in a unique cyberinfrastructure, all the fundamental textural and petrological information of the metamorphic rocks.

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# Geological Map of Forenza Town Area (prov. of Potenza), 1:15.000 scale. External Sector of Southern Apennines

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Keywords: Southern Apennines, Tufillo-Serra Palazzo unit, Daunia unit.

The stratigraphic and structural characters of the external sector of the Lucanian Apennines were studied, through the realization of a Geological Map at 1:15.000 scale. The geological map has been obtained through five working steps: 1) recovery of basic topographic map and creation of a GIS project; 2) bibliographic study; 3) geological survey in the field; 4) input and processing of data through OGIS software; 5) graphic layout of the geological map through Illustrator CS3. The GIS project, created for storage and data processing, has been implemented with the regional technical map (CTR) at 1:10.000 scale (maps N° 452100, 452110, 452140, 452150; R.S.: WGS 84), the orthophotos at 1:5.000 scale (resolution:20 cm) and the digital terrain model (resolution: 5 m), becoming a powerful work tool for the logistic planning of the field activity in a mountainous area, interpretation, storage and processing of data. In fact, during the geological survey planning and the processing phase, the use of the digital terrain model gave great advantages in the identification, interpretation and mapping of the most important stratigraphic and tectonic elements. In the chain area, three Tectonic Units have been distinguished, represented from top to bottom by: 1) the Sannio Unit, SU (Patacca& Scandone, 2007), represented in the study area only by the Numidian Flysch, FYN (Ogniben, 1969); 2) the Tufillo-Serra Palazzo Unit, TSU (Patacca& Scandone, 2007), represented in stratigraphic order by the Flysch Rosso, FYR (APAT, 2007), Numidian Flysch, FYN (Ogniben, 1969) and the Serra Palazzo Formation, PAA (Selli, 1962); 3) the Daunia Unit, DU (Patacca& Scandone, 2007), consisting of the Flysch Rosso esterno, FYRe (APAT, 2007) passing upwards to the Flysch diFaeto, FAE (Crostella & Vezzani, 1964). The data collected in the field have highlighted some differences with the pre-existing cartography, such as: i) the identification for the first time of the FYRe (related to Monte Sidone Formation) in the south western area of the Forenza town; ii) the definition of a east verging thrust which superimpose the TSU on the DU and the related footwall syncline, whose overturned limb outcrops along M. Armenia-Forenza high; iii) the mapping of west verging thrusts(apennineback-thrust) in the western sector of the TSU.

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#### **Regional scale morphotectonic pattern of the Tyrrhenian Sea**

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Keywords: EMODnet, Morpholineaments, Regional Tectonics.

Digital Elevation Model (DEM) data analysis has been applied in several environmental and geological studies. At a regional scale, morphological analysis has been applied to detect tectonics affecting onland surfaces, based on the analysis of morphological lineaments (Burbank and Anderson, 2001). The interpretation of seafloor morphological lineaments and their relationship with tectonics is less advanced, due to the scarcity of high resolution data available at regional scale. This work shows the results of a combined use of DEM analysis on swath bathymetry and on tectonics in order to investigate from a morphotectonic viewpoint the seabottom features in the Tyrrhenian Sea.

The morphology of the entire Tyrrhenian Sea has been analysed based on middle resolution multibeam bathymetry and on 100 m-contour lines (scale), part of a "Tyrrhenian project" (Marani et al., 2004). A first morpholineaments map has been created identifying more than 500 features > 10 km in length, without considering their tectonic settings and the timing of their development. Furthermore, a Tyrrhenian regional tectonics map has been digitized from literature. Maps 1:1.500.000 (Ambrosetti et al., 1987) and 1: 500.000 (Barone et al., 1983) were used to extract a faults network.

Morpholineaments and tectonic lineaments have been grouped in six Tyrrhenian Sea geographical zones and plotted in rose diagrams in order to obtain the main trends in each region. Rose diagrams show that most of the identified morpholineaments have a tectonic origin, although they are not coeval, as they developed during different phases of the opening of the Tyrrhenian back-arc basin. Results suggest that the Northern, Western and Central Tyrrhenian are dominated by a main trend, controlled by extensional tectonics related to the progressive retreat of the slab subduction, in contrast, the occurrence of several trends in the Eastern and Southern Tyrrhenian suggests additional tectonic complexities in those regions.

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## The pre-Pliocene geological map of the Adriatic Sea

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Keywords: Geological map, Adriatic sea, EMODNet.

In the framework of the EMODNet project, the realization of a prototype map representing the pre-Pliocene substrate of the Adriatic area has been start.

The Adriatic represents an area of high complexity, being divided into numerous sectors characterized by different geological complexity:

- the Adriatic foredeep (parallel to the structural axes of the Apennines, subdivided into some distinct depocenters);
- the Adriatic foreland (Colli Euganei and Istria peninsula);
- the imbricated style Adria margin (Venetian Alps, Mura depression, Central Dalmazia);
- the vast circum-Adriatic area (Eastern Alps and Northern Croatia);
- the Albanian transition (Albanides from the Dinarides to the Hellenides).

The realization of the map affords for the collection of information on the pre-Pliocene substrate available in the analog or digital archives of the peri-Adriatic countries Geological Surveys derived from published and unpublished scientific literature.

The map processing requires the representation through isobaths of the bottom surface of the Pliocene deposits, whose depth is calibrate using the boundary depth available from deep boreholes stratigraphic logs or from seismic lines developed for oil exploration or for scientific purposes.

The map will represent the polygons relative to the identified geological units, attempting an initial approach on semantic and geometric harmonization, following the Work Package 4 guidelines of the EMODNet project.

The structural elements will symbolize the deformation structures affecting the substrate, thus excluding the Pliocene-Pleistocene tectonic lines.

Then, the pre-Pliocene paleomorphology will be study with the aim of defining the main morphotectonic elements and identifying the Pliocene evolution of the Adriatic area.

The goal of this work is to bring together an interdisciplinary group of scientists working in the peri-Adriatic countries to identify areas of consensus as well as unresolved questions about the knowledge of the substratum geology of the Adriatic Sea area.

This work represents, therefore, an important example of trans-national cooperation involving all the Geological Survey organizations of the countries facing on the Adriatic Sea.

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# Characteristics of the 2016 central Italy earthquake surface ruptures (M 6.5) from detailed digital mapping: rupture parameters and comparison with global data

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Keywords: 2016 earthquakes, central Italy, normal fault.

The 2016 seismic sequence began on August 24 with a Mw 6.0 event located 9 Km NW of the Amatrice town. A Mw 5.9 event occurred on October 26, located 25 km further N. The main shock (Mw 6.5) occurred 5 km from the Norcia town on October 30. The first event nucleated between the Mt. Gorzano and Mt. Vettore faults, while the second and the third shocks nucleated on the Mt. Vettore - Mt. Bove fault system. All are normal faulting earthquakes on SW-dipping faults. The Open EMERGEO research group (Civico et al., 2018) performed the survey of coseismic effects starting few hours after the main events. The northern area of the fault system was only partially surveyed by Open EMERGEO. Therefore, we performed additional field work in order to fill in the gaps of rupture mapping/measuring and obtain more complete estimates of the surface displacement. We used techniques of digital mapping (FieldMove application developed by Midland Valley, in particular with a touchscreen tablet device with the iOS operating system).

The collected data allowed us to reconstruct the along-strike displacement profile and the main rupture parameters. These parameters are the Average Displacement (AD), the Maximum Displacement (MD) and the Surface Rupture Length (SRL). The results obtained are: SRL 30 Km; Arithmetic AD 37 cm; Integral AD 36 cm; Geometric AD 36 cm; MD 240 cm.

The comparison with global normal faulting data shows that the AD is lower than the value expected from empirical relations, the MD is higher than the expected value and the AD/MD ratio is lower than global data. A possible explanation for the low value of AD is an attenuation of coseismic displacement toward the surface, possibly due to the high segmentation of the fault-system. The long-term (post-Late Glacial Maximum) AD/MD ratio is more close to the global coseismic data, suggesting that the AD/MD ratio is recovered during the long-term, possibly due to moderate-magnitude earthquakes on single fault sections, or creep processes or both of them. The anomalously high value of MD might be partially due to localized tectonic phenomena, such as back-tilting. The realization of high-resolution topographic profiles allowed us to calculate the long-term vertical slip rate and to compare the topographic displacement profile with the coseismic displacement profile along the fault system. The good correlation between the coseismic MD and topographic MD suggests that the maximum displacement recurs systematically in the same section of the fault.

Acknowledgments: Work partially funded by the studentship "Your heartquake makes the difference" issued by Società Geologica Italiana and Bergamo Scienza Association.

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#### UAV assisted geological mapping: application to stratigraphy and structural survey

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Keywords: Geomatics, Stratigraphic columns, Triangle zone structures.

Following previous researches and experiences (Casella et al., 2017; Martinez et al, 2017; Nieminski et al. 2017), some experimental tests were carried out during Digital Geological Survey (Geological Sciences MSc.) and Geomatics (Applied Information technology BSc) courses at Urbino University. During the last year field activities students and researchers tested the use of UAV (unmanned aerial vehicle) both commercial (DJI Phantom 3) and in-house built machine.

Because of the reliability, we choose to perform our survey tests using the commercial one.

After having digital field mapped an Apennines area where the Miocene turbidite Marnoso Arenacea Formation crops out (Marche- Tuscany border), we choose to fly on top of two already tape measured stratigraphic sections. After some flight we were able to built orthophotos and DEM with points clouds (using Agisoft Photoscan) that could be imported in QGIS 3.0 where we measured the stratigraphic columns, highlighting bedding and key strata. As pros of tape measurement is the direct contact with bedding allowing more accurate observations. In the other side, as cons, the unsafe measurement on vertical cliffs (performed with climbing techniques) can be avoided with reliable remote measurements without noticeable deviations.

Moreover we tried to build a 3D geological model of a quite complex triangle zone associated to a main thrust. The UAV flew manually controlled along a creek where the deformed and faulted beds crop out. The very detailed points cloud allowed to draw and build an interpretative model.

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# Joining field mapping, subsurface stratigraphy and geological history in comprehensive 3D geological models: hints from the Quaternary Po Basin (Lombardy, Italy)

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Keywords: 3D geological models, geological map, Po Basin.

Surface and subsurface geological characterization of Quaternary alluvial basins is important in many geological applications, including geohazard evaluation, exploitation and protection of natural resources. In these settings, subsurface models are best performed if the 3D stratigraphic architecture is described, accounting for the hierarchy of the sedimentary bodies, which depends on the duration and intensity of depositional/ erosional processes and on the syn- to post-depositional deformation history. However, geological modelling is affected by relevant uncertainty owing to lack of information, as the subsurface is usually investigated from irregular sampling points, and hard handling of structural elements. Aiming to improve the integration of surface and subsurface reconstructions into reliable 3D and evolutionary models, we chose to study a sector in the southern Po Plain of Lombardy (San Colombano Hill area, 30 km S of Milan), where Apennine tectonics affected the Quaternary stratigraphy of alpine-sourced shallow marine to alluvial sediments. A new reconstruction of the Quaternary geology of the area, and the proposal of a methodology to deal with all the available surface and subsurface data into a comprehensive 3D geological model, is the result of this stage of the work. Original geological and geomorphological mapping at 1:10.000 was followed by digitization of normalized subsurface log data (water wells, boreholes, geophysical soundings, average depth 150 m bgs), based on a specifically-built litho-textural Code. Field-based data were combined with 1D facies analysis of subsurface logs and correlated into a fence of 2D geological cross-sections. New GIS tools were implemented to predispose the multi-scale dataset to 3D analysis using ad-hoc built hierarchic and thematic geo-Databases. The new surface maps and cross-sections allowed to constrain the 3D reconstruction to the data-points and to both the hierarchic architecture and the geological evolution. The 3D model was processed by interfacing the GIS management with the 3D GeoModeller® software, which implements the potential field method, to rapidly simulate and visualize the stratigraphic/tectonic relations, honoring the mentioned geological and evolutionary constraints. Several forward models were computed to compare different and even contrasting architectures and evolutions, and some hints are proposed to deal with the geological hierarchy, at present not encompassed in the GeoModeller® suite. The alternative 3D models contribute to better define the geometries of the stratigraphic units and tectonic features, to check the geological maps and sections, to discuss the evolution of the Quaternary Po Basin during the latest Apennine tectonics. This work suggests an integrated methodology to manage heterogeneous geological data, feasible and applicable to many comparable geological contexts, joining geological mapping, analogue analysis and mathematical modelling.

# **Session S8**

# Tectonic and sedimentation relationships in Mediterranean basins and belts. A tribute to Fabio Lentini

Conveners AND CHAIRPERSONS Agata Di Stefano (Università di Catania) Rosanna Maniscalco (Università di Catania)

#### Evidence for a Late Tortonian Wedge-Top Basin in the Northern Rif Belt (Morocco)

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Keywords: Rif belt, Wedge-top basin, Biostratigraphy.

We report on new stratigraphic data concerning Middle - Upper Miocene deposits outcropping in the Northern Rif Belt. We analyzed sections located in the Dar Zhiro-Bougdour and Saf Lahmam-Seguedla areas, 30 km to the south of Tanger City. In these regions, sandy-clayey deposits unconformably overlie the Numidian and like-Numidian (quartz-lithic arenites) successions pertaining to the Massylian and the External Tanger Intrarif sub-domains, respectively. In turn, the Massylian sub-domain belongs to the Maghrebian Flysch Basin (MFB), whereas the External Tanger Intrarif is part of the External Rif domain (ER).

The tectono-stratigraphic features of the studied areas, e.g. the basal unconformity and the slight compressional deformation with respect to the substratum, let us to refer them to a wedge-top basin recording the compressional deformation of MFB and ER domains.

Dar Zhiro-Bougdour and Saf Lahmam-Seguedla sections are both represented mainly by dm-thick turbiditic strata interbedded with light-colored and bluish/pinkish marls. These successions show sulfur nodules, glauconie, and ichnofacies pointing to a deep marine environment.

Biostratigraphic quantitative analyses, performed on calcareous nannofossil assemblages, provided ages ranging from latest Serravallian to Tortonian for Saf Lahmam-Seguedla areas, and late Tortonian for Dar Zhiro-Bougdour.

The new stratigraphic results are a major constraint for the closure timing of the Maghrebian Flysch Basin and its tectono-sedimentary evolution, which is coeval with the internal part of the Intrarif sub-domain. Particularly, they point out the latest collisional and docking stages of the whole Rif nappe-stack onto the African plate in the Gibraltar Arc system.

# Variability of Africa-vergent Fold-and-Thrust Belts and Foreland Basins of the Central Mediterranean: The Inheritance of Mesozoic Palaeogeography

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Keywords: foreland basins, fold-and-thrust belts, Mesozoic palaeogeography.

The lithospheric strength and the load of the fold-and-thrust belt are considered as the main controlling factors in shaping foreland basins. Nevertheless, a review of the Cenozoic foreland basins resting on the African margin, and in particular the basins surrounding Adria, shows that thickness, depocentral geometry and sedimentary facies of these basins vary remarkably along strike. The Mesozoic palaeogeography of the southern Tethyan margin is characterised by a system of carbonate platforms and epicontinental basins passing to adjacent oceanic basins, belonging to various branches of the Tethyan ocean s.l. Following the consumption of the Tethyan oceanic domains, subducted during the Africa-Eurasia convergence, the sedimentary successions of the southerm Tethyan margin were progressively involved in thrusting and folding, giving rise to a system of foreland basins that fringes Adria along the Dinarides-Hellenides, Southern Alps, and Apennines, continuing into the Sicilian Maghrebides. The structural style in the frontal part of these fold-and-thrust belts appears to be controlled by the different lithomechanics of the Mesozoic sedimentary successions, and therefore it likely reflects the articulate palaeogeography of the Mesozoic domains of the southern Tethyan margin. Almost everywhere the structural style of the fold-and-thrust belt and the features of the adjacent foreland basin show a close correlation with the Mesozoic palaeogeographic domains in the foreland. In particular, it appears that inherited topographic depressions in the foreland represent preferential sites of clastic sediment accumulation, whereas foreland basin sedimentation can be largely reduced above the domains of Mesozoic shallow water carbonate platforms. These relationships can be documented in the Southern Alps retro-wedge foreland basin system of Oligo-Miocene age, as well as in the pro-wedge foreland basin systems of the Northern and Southern Apennines, of the Sicilian Maghrebides and of the Hellenides-Dinarides. The relationships observed in the recentmost foreland basins allow to make use of the structural and sedimentary features of the older foreland basin sediments, currently stacked within the fold-and-thrust belts, to make inferences on the Mesozoic palaeogeography of the southern Tethyan margin.

# From foredeep to wedge-top in the Plio-Pleistocene Bradano basin: the Apulia plate as the external front of the Southern Apennines and the Calabrian Arc. Implications for seismic hazard in the Gulf of Taranto

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Keywords: Southern Apennines, Calabrian Arc, Apulian plate.

Multi-scale, high-resolution seismic reflection profiles combined with exploration wells and seafloor bathymetry were used to describe the structural and morphostructural setting of the Gulf of Taranto, in the northern Ionian Sea, in order to unravel its tectono-sedimentary evolution during the Pliocene-Pleistocene. Being located between the Ionian Calabrian Margin, to the West, and the Apulian Margin, to the East, the Gulf of Taranto is the site of pervasive tectonic deformation as part of a complex orogenic system that includes five main domains: the Calabrian Arc, the Calabrian Accretionary Wedge, the Southern Apennines and the subducting Apulian Foreland Ramp. Across-strike transcurrent fault zones segment all the above-listed domains. The external fronts of the Calabrian Accretionary Wedge and Southern Apennines progressively migrated toward the ESE overriding and colliding with the subducting Apulia and Ionian lithospheres during the Neogene and Quaternary (Rossi et al., 1983). The collisional setting has been responsible for the formation of the Bradano Foredeep Basin, whose offshore portion is located in the Gulf of Taranto. Various studies revealed that the Apulian Foreland Ramp was uplifted, down-flexed toward west and associated to contraction and transcurrent deformations along E-W trending faults active since the Miocene until recent times (Pieri et al., 1997). In this integrated study, it is shown that thrusts and thrust-related anticlines affected the whole Apulian Foreland Ramp, even underneath the Southern Apennines. Thrust-related folds strike NW-SE and N-S, likely following inherited Mesozoic-Pliocene(?) extensional faults, which might be responsible also for the gentle folding of the Pliocene-Recent deposits. These deep thrusts form very open anticlines, suggesting collision and shortening across the lower Apulian plate, which, in such case, should be considered part of the Apenninic orogenic wedge.

The results of the study suggest that during the Pleistocene 1) the Bradano basin ended to be a foredeep basin and it became a wedge-top basin; 2) the Apulia foreland ramp contained the outermost fronts of the Southern Apennines and Calabrian Arc orogenic wedges. The occurrence of basement-involving and positively-inverted extensional faults affecting the Apulian plate allow to reconsider the assessment of the seismic hazards of this highly populated area along the coast around the Gulf of Taranto.

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# New information from "old" seismic lines: an updated geological interpretation from the re-processing of the CROP line M-2A/I (Bonifacio Straits) at shallow depth

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Keywords: Seismic interpretation, Bonifacio straits, CROP Project.

The shallowest part (about 3 sec two-way traveltime) of the CROP line M-2A/I, acquired during 1991 in the Bonifacio Strait (between Corsica and Sardinia), has been reprocessed to improve its geological interpretation. The original target of the M-2A/I profile was the entire crust and therefore the shallowest part was only partially interpreted. In this context, the re-processing procedure was carried out to improve the signal-to-noise ratio and the resolution of the M-2A/I seismic profile at shallow depth. The geological interpretation of the reprocessed data aimed at the reconstruction of the sedimentary succession and the contact with the underlying Hercynian basement.

The M-2A/I seismic profile has been interpreted identifying diverse seismic facies, interpreted considering the geological units outcropping to the north (in Corsica) and to the south (in Sardinia) of the seismic profile. The re-processing procedure improved the signal-to-noise ratio and the resolution of the seismic images, supporting the identification of different seismic facies: regional geology and the geometry of the reflectors in the re-processed lines support a correspondence between geological units cropping out in the surroundings of the seismic line and the seismic facies. The study supports the existence of a thick Mesozoic succession, onlapping the Hercynian basement, preserved below the Cenozoic succession in the Asinara Gulf, suggesting that the Nurra succession continues northward below the sea. The Mesozoic succession is bordered by a major, east-dipping normal fault, east of the Asinara Island ridge. The faults recognized in the seismic profile indicate a prevailing strike slip/transtensional tectonics, questioning the role of compressional tectonics suggested in a previous interpretation.

The re-processing of the seismic line with the proposed work-flow significantly improved the quality of the seismic image with respect to that obtained in the past. In addition, the improved regional geological knowledge permitted a more reliable correlation of the seismic facies with the lithological units exposed on land. The results obtained by this joint effort clearly indicate that the re-processing of existing seismic lines, partly «forgotten» after their original use, represents an important resource for improving the geological knowledge without acquiring new, expensive seismic data thanks to the development of new processing procedures and to the continuous upgrade of the regional geological knowledge.

### Stratigraphic and structural characterization of the Roccacaramanico Conglomerates (Majella Unit - Abruzzo, Italy)

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Keywords: Physical stratigraphy, lower Pliocene, Roccacaramanico Conglomerates.

In the pelitic-arenaceous foredeep succession of the Majella Unit, a coarse grained, calcareous-clastic composite bed, known in the literature as Roccacaramanico (RCC) or San Valentino Conglomerates, marks approximately the Miocene-Pliocene boundary. Its deposition is referred to high density gravity flow mechanisms. The RCC has been extensively mapped in the area of the Torre De' Passeri (360) and Sulmona (369) sheets of the Carta Geologica d'Italia (CARG Project). Micropaleontological data constrained its stratigraphic position within the Sphaeroidinellopsis sp. Biozone, very Early Pliocene.

Nevertheless, the RCC has never been analysed in detail for what concerns its physical stratigraphy, composition and style of deformation during the Late Pliocene folding and thrusting.

We present the results of a study carried out in two exposures of the conglomerates, located in the type area close to the Roccacaramanico village. The analysed sections revealed that the RCC consists of several (six to nine) amalgamated layers, distinguished on the basis of grain size and textural vertical variations. The basal layer is very coarse grained and includes rounded pebbles scattered in a sandy-gravelly matrix. At its bottom, groove and flute casts, indicate the southern provenance of the sedimentary flow which fed the beds. The visual inspection of some polished samples collected at various height within the RCC, and the subsequent microscopic analyses in thin section, highlighted an almost pure calcareous composition, with very rare siliciclastic clasts. Anyhow a wide range of limestone types, characterized by shelf, basinal and slope facies was documented. The latter allowed us to make inferences on the source areas of the detrital supply and the degree of exhumation of the tectonic pile stacked at the rear of the foredeep when the RCC settled. A further reason of interest of RCC, in the Roccacaramanico area, concerns its structural setting. In fact, the two study sites are localized in the internal (i.e. western) overturned limb of a syncline, developed in the footwall block of the Mt Morrone and La Queglia thrusts, a few hundreds meters below the latter. Due to the strong contrast of competence with the predominantly pelitic flysch-type deposits laying above and below, the RCC suffered intense deformations. The resulting structural assemblage consists of sets of pressure solution cleavage, fracture cleavage, joints and mesofaults causing displacements in the range from some centimeters to some meters. The bed is also affected by folding around two very distinct axial directions: a primary trend which is sub-parallel to the regional-scale thrust and folds; a secondary trend which causes local sharp deflections at high-angle respect to the former. A conceptual model, explaining the origin of this fracturing and folding pattern, in response to the progressive shearing induced by the overhanging Mt Morrone and La Queglia thrusts, is finally elaborated.

#### Interactions between tectonics and deposition in thrust-related basins: interpreting the record

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Keywords: thrust-top basins, tectonic reconstruction, palaeogeography.

The stratigraphy of syn-orogenic sedimentary rocks provides unparalleled information on long-term rates of tectonic processes. However, sediments deposited across and ahead of evolving structures can influence their evolution. "This kind of research... [requires]... close co-operation between stratigraphers, sedimentologists and structural geologists" (Mutti et al. 2009), words coined to express doubt on possible progress in understanding how deformation of the sea-bed can control facies distributions in turbidites that are generally applicable to all tectono-stratigraphic settings. Many idealised depositional models are simply inappropriate for understanding sedimentary processes and facies distributions for systems that accumulated within tectonically active sedimentary basins. Examples here are drawn from outcrops across the Mahgrebian thrust systems of Sicily - applying insights gained worldwide from interpreted high-resolution marine seismic data that provide abundant analogues for depositional architectures, facies associations and their relationship to structural geometry. In general, structural evolution is strongly influenced by deposition across thrust wedges, damping fold amplification, influencing wedge migration and especially the climb of the frontal thrust. Thus emergent thrust systems (e.g. Apennine-Mahgrebian) have a different range of structural geometries compared with their buried counterparts that typify outcrop of many ancient orogens (Appalachians, NW Highlands, internal Alps). The depositional records of thrust-top basins place important limits on interpretations of thrust displacements - generally excluding those that require long-range exotic thrust sheets. As long known from tectono-geomorphological studies in subaerial basins, structures within the thrust wedge can exert a primary control on sediment routing. In submarine systems, similar interactions are recorded by turbidites - exemplified by the Numidian sands that accumulated now outcropping in Sicily and the southern Apennines. Likewise active fold amplification strongly influences coastal processes, tuned by high-frequency eustatic sealevel cyclicity, and this is exemplified across the thrust wedge of Sicily, not only by the stratigraphy of Messinian strata but also the stacking patterns of Plio-Pleistocene packstones. Collectively these studies provide important tests on the validity of tectonic models and challenge many extant palaeogeographic reconstructions.

This contribution is dedicated to the memory of Fabio Lentini who did so much to create tectono-stratigraphic understanding in Sicily and the southern Apennines.

### Impact of Neotethys's rifting on Western Desert basins evolution

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Keywords: Egypt, Kattaniya Fault, Rosetta Fault, rifting.

Egypt has been one of the most productive countries of North Africa, with three main petroleum provinces: Gulf of Suez, Nile Delta and Western Desert.

The first one, it's linked to the opening of the Red Sea (Oligocene-Pliocene), the second one by the deposition of paleo-Nile delta and finally, the Western Desert developed following the Mesozoic extensional tectonic.

The Western Desert is one of the world's most prolific Jurassic and Cretaceous hydrocarbon province, characterized by many basins that experienced organic-rich sedimentation at different times, including the late Cenomanian/early Turonian referred to as oceanic anoxic event (Dolson et al., 2014).

More in particular, Western Desert is characterized by the presence of five main large sedimentary basins suggesting a progressive rejuvenation of the main phases of subsidence from West to East: Faghur (Paleozoic-Tertiary), El Alamein - Shushan (Jurassic-Oligocene), Matruh (Early Cretaceous-Tertiary), Abu Gharadig (Late Cretaceous-Tertiary) and Gindi (Eocene).

The evolution and the geometry of these basins were controlled by the presence of some NE-SW trending regional faults: Rosetta and Kattaniya fault systems. In particular, Rosetta fault system led the evolution of El Alamein Basin, and may be Faghur basin<del>s</del>, whereas Kattaniya fault system led the evolution of Abu Gharadig basin.

The Hercynian Orogeny and Neotethys tectonic activity (Cavazza et al., 2004) influenced the evolution of Western Desert from Paleozoic to Cretaceous. In fact, the Permian-Mesozoic rifting, caused the formation or reactivation of many transform faults that may have conditioned the tectonic evolution in the northern part of African craton. Comparing the location of the Transform Faults since Late Permian to Cretaceous and the Rosetta and Kattaniya faults, we propose that Rosetta and Kattaniya faults represent the continuation of transform faults on the North African craton. Some elements as the direction, the age of the basins and the subsidence migration from West to East may be in relation with the opening of the Neotethys

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## Stratigraphic and structural complexity in the Northern-Central Apennines: the record of the geological sheet Antrodoco, 1:50.000 scale

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Keywords: Antrodoco sheet, geological complexity, paleo-tectonic.

The Servizio Geologico d'Italia (SGI) has recently completed the mapping of the Geological sheet Antrodoco, 1:50.000 scale. The area includes the NW portion of Latium-Abruzzi (L-A) Platform and the surrounding Umbro-Sabino (U-S) and Gran Sasso (G-S) Basins, and is crossed by Olevano-Antrodoco-Sibillini (OAS), M. Gabbia and M. Mozzano thrusts, and by Pizzoli and Montereale active fault systems.

The high geological complexity of this area has led to map more than 60 marine units, related to different geodynamic contexts and various environments, ranging from inner platform to basin, spanning from Late Triassic up to Pliocene. Several continental units are related to the evolution of six Quaternary intermountain basins.

These units recorded six pre-orogenic extensional tectonic phases (Early Jurassic, Bajocian, Turonian-Coniacian, Late Paleocene, Late Eocene and Late Miocene in age) the Late Miocene-Early Pliocene compressional phase and the last Quaternary extensional phase.

The Early Jurassic rifting caused the onset of the L-A Platform and the U-S and G-S basins hosting pelagic carbonate platforms (PCPs), four of these have been identified in the area. Unlike the latter, the M. Giano PCP has formed during Bajocian and has been newly catch up by Tithonian shallow water facies.

The Late Cretaceous and Paleogene tectonic phases caused, together with eustatic and biological factors, the drowning of the NW portion of the L-A Platform and the creation of a complex paleotopography.

The Late Miocene extensional tectonic, related to the peripheral bulge flexuration, created confined foredeep basins (e.g. Antrodoco basin) through some major faults that show a remarkable peak-type displacement. Miocene normal faults often re-used Jurassic faults and escarpments (e.g. M. Boragine and M.Marine-Pizzoli faults).

The Upper Miocene-Early Pliocene compressional orogenic phase was responsible of the definition of three main thrust systems: the Monti Reatini portion of the OAS thrust, the M. Gabbia and M. Mozzano thrusts.

The compressional deformation developed mainly through a progressive/synchronous thrusting, re-using or cutting previous structural elements. The final result is an articulated structural pattern, with apparent youngeron-older thrusting, rotations and positive inversion of paleo-faults, buttressing and back-thrusting phenomena. Very often the compressive deformation does not seem to produce important stratigraphic throws and in some case, as in the western part of M. Gabbia thrust, does not seem to break-through. This does not exclude important horizontal displacements at depth, as testified by the Antrodoco1 well.

The final extensional Quaternary tectonic re-activate the previous structural elements, preferably Miocene, when compatibles with the NE-SW oriented  $\sigma$ 1, or originated new faults.

### The stratigraphic evolution of a submarine channel system in a tectonically-confined basin: the Miocene Gorgoglione flysch formation, southern Italy

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Keywords: basin structural confinement, Southern Apennines, submarine channels.

The Gorgoglione Flysch Fm is a siliciclastic deep-marine succession developed during the Miocene in an elongate thrust-top basin of the Southern Apennines (Italy). The stratigraphic product of protracted sediment transfer and deposition through a long-lived channel system is recorded in a wide outcrop belt, nearly 500 m thick and 15 km long, oriented oblique to the regional palaeoflow. These exceptional exposures of channel-fill strata allow the stacking architectures and the general evolution of the channel system to be analysed at multiple scales, enabling the effects of syn-sedimentary thrust tectonics and basin confinement on the depositional system development to be deciphered. An approach based on the integration of standard sedimentary facies analysis and emerging digital techniques for outcrop mapping has been employed to enhance the interpretation of the multiple levels of submarine channel hierarchy. Two end-member types of elementary channel architecture, each consisting of a distinct internal facies distribution and associated outof-channel deposits, have been identified: (i) high aspect-ratio, weakly-confined channels flanked by sandprone heterolithic deposits; and (ii) low-aspect-ratio, incisional channels flanked by mud-prone heterolithic deposits. Their systematic stacking results in a complex pattern of seismic-scale depositional architectures that determines the stratigraphic framework of the deep-water system. From the base of the succession, two prominent channel-complex sets have been recognized, namely CS1 and CS2, consisting of amalgamated incisional channel elements and weakly-confined channel elements, respectively. These channelized units are overlain by isolated incisional channels, erosional into mud-prone slope deposits. The deposition of different channel architectures is interpreted to have been governed by regional thrust tectonics combined with a high subsidence rate that promoted significant aggradation. In this scenario, the alternate in- and out-of-sequence tectonic pulses of the basin-bounding thrust structures controlled the activation and deactivation of the coarseclastic inputs in the basin. The tectonically-driven confinement of the depositional system limited the lateral offset in channel stacking, preventing large-scale avulsions and the development of superelevated levees. This study should find wide applicability in analogous depositional systems in the subsurface, whose hosting architecture has been influenced by tectonically-controlled lateral confinement of the basin and associated lateral tilting.

# The Middle Jurassic evolution of the Central High Atlas domain (Morocco): suggestions from the paleo-drainage evolution of the Guettouia Formation

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Keywords: Central High Atlas, Paleo-drainage, tectonic and sedimentation.

The High Atlas is an orogenic system resulting from the Cenozoic-Recent tectonic inversion of Triassic-Jurassic rift systems. Its present setting derives from a long and complex tectono-sedimentary evolution related to the Early Mesozoic opening of the Atlantic Ocean (pre-orogenic period) and, then, to the Cenozoic convergence between the African and European plates which led to a full tectonic inversion (orogenic period; Frizon de Lamotte et al., 2008, 2009). The WSW-ENE trending chain is bounded by the North Atlas Fault to the north and the South Atlas Fault to the south, that represented the master faults of the rifted basins during the pre-orogenic period, then reactivated in inversion during the orogenic period. Early Jurassic syn-rift carbonate platforms related to a marine ingression, were replaced in the Middle Jurassic-Late Cretaceous by post-rift fluvial and lacustrine environments. The related continental successions, regionally known as *Couches Rouges* (Jenny et al., 1981; Haddoumi et al. 2010), are not unanimously interpreted in the frame of the tectono-sedimentary evolution of the High Atlas. According to some authors they record localized early compressive-transpressive stages of deformation (Laville 1985; Piqué et al. 1998; Benvenuti et al. 2017; Cavallina et al., 2017; Moratti et al., 2018), others refer them to a period of tectonic quiescence (Beauchamp et al. 1999; Teixell et al. 2003; Tesón and Teixell, 2008; Frizon de Lamotte et al., 2008, 2009).

This study illustrates a revised stratigraphy, facies analyses and paleo-drainage reconstruction of the Guettouia Formation (late Bathonian, Charrier et al., 2005), that represents the first continental unit of the *Couches Rouges*, outcropping at the core of several syncline basins throughout the Central High Atlas. The aim is to understand if there was a tectonic forcing on the development of the Middle Jurassic fluvial systems.

The sedimentological characters observed in the Guettouia formation suggest that it was deposited by wide ephemeral fluvial systems, characterized by a high variable discharge (*sensu* Plink-Björklund, 2015), separated by local thresholds. In the High Atlas of Marrakech, the western part of the study area, these rivers flowed to the north, towards the shoulders of the paleo-rift (Cavallina et al., 2017). Moving to the east, the fluvial systems gradually become parallel to the axes of the paleo-rift, flowing to East-Northeast. Our reconstruction suggests that the post-rift fluvial systems, represented by the Guettouia F., were controlled by the presence of a topographic high in the area of the High Atlas of Marrakech, forcing the fluvial systems to flow towards and possibly beyond the shoulders of the paleo-rift. This conclusion, together with structural data and tectonic observations collected in the study areas, supports the idea that, from the Middle Jurassic, the Central High Atlas were affected by early compressive-transpressive stages of deformation.

### Tectonic control on trench-type basin stratigraphic succession in Apenninic-Maghrebian Orogen. An example from the Tufiti di Tusa Formation (Calabria - Lucania border, Southern Italy)

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Keywords: Apenninic-Maghrebian Orogen, trench-type basin, Tufiti di Tusa Formation.

The aim of this communication is to discuss the influence of synsedimentary tectonic activity on the stratigraphic succession of the Tufiti di Tusa Formation, belonging to a late Paleogene trench-type basin located on the westward subducting Tethyan-Adria lithosphere (e.g. Carminati et al., 2012). This formation features volcanoclastic turbidites consisting mainly of K-calc-alkaline detritus, referable to a magmatic arc active in the central Mediterranean region during Eocene - early Miocene (e.g. Lentini, 1979; Perri et al., 2012; Cerone et al., 2017). Detailed facies analyses performed on the Tufiti di Tusa sedimentary succession along the Cappozzolo river (close to the Calabria-Lucania border) point out remarkable changes in the vertical facies distribution allowing three different stratigraphic units to be defined, which, from bottom to the top, are: i) (0-60 m) tabular contained-reflected quartzolithic and calciclastic fine-grained turbidites, referable to a confined distal depositional environment with morphologic irregularities; ii) (60-95 m) tabular mainly-volcanoclastic coarse to fine-grained turbidites interpreted as slurry beds or hybrid event beds, the increase of which can indicate a synsedimentary tectonic control of the basin morphology (e.g. Haughton et al., 2009; Tinterri & Muzzi Magalhanes, 2011); iii) (195-230 m) thick bedded coarse-grained massive volcanoclastic turbidites suggesting the growing of important structural highs. On the whole, the vertical distribution of the study section facies associations can be interpreted as recording the main structural events related to a progressive uplift and closure of the basin.

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# Unconformities, neptunian dykes and mass-transport deposits as an evidence for synsedimentary tectonics: new insights from the Central Apennines

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Keywords: Early Cretaceous normal faulting, Umbria-Marche-Sabina Basin, Jurassic PCP-basin systems.

This work presents the results of a geological mapping project (1:10.000 scale) performed on the Narni-Amelia Ridge (Central Apennines, Italy), a sector of the Umbria-Marche-Sabina (UMS) domain. Fieldwork was aimed at defining the rift and post-rift architecture of the Jurassic-to-Cretaceous part of the UMS basin succession. Restoring the local Jurassic rift-related pelagic carbonate platform (PCP)/basin pattern served as a starting point to constrain the post-Early Jurassic tectono-sedimentary evolution of the study area. The existence of PCP-basin systems is evidenced by lateral thickness and facies variations of Jurassic-Lower Cretaceous deposits. These differences generally faded out as the Maiolica Fm. leveled the submarine rift topography. The Narni-Amelia Ridge makes an exception as it carries direct and indirect evidence for a late Early Cretaceous phase of renewed extension. This is testified by:

i) the occurrence of polygenic, chaotic megabreccia deposits ("Mt. Cosce Breccia"). The clasts are made of Jurassic-Lower Cretaceous deposits derived from condensed PCP-top, PCP-margin and basinal successions, while the matrix is Maiolica-type facies. These deposits rest unconformably through an erosional surface on the Jurassic (and Cretaceous) horst-block. Stepped unconformities are associated with "spur and groove" geometries of the escarpment, suggesting topographic backstepping due to rock-fall processes. Production of the "Mt. Cosce Breccia" was triggered by Cretaceous faulting, which caused a retreat of the Jurassic margin of the Mt. Cosce PCP, rejuvenating the submarine paleotopography.

ii) millimeter-to-decameter-scale neptunian dykes and sills made of "Mt. Cosce Breccia" and of Maiolica pelagites. Fractures cut the footwall-block of Cretaceous faults, made of Calcare Massiccio Fm. (Hettangian), sub-orthogonal to its master-bedding. Dykes are associated with tension gashes filled not with pelagites or calcite, but with chert (silicification of fracture zones). Silicification of the Jurassic bedrock characterizes the steep walls of those neptunian dykes filled with cherty Maiolica-type deposits.

iii) the onlap of Aptian-Albian Marne a Fucoidi Fm. onto the Hettangian Calcare Massiccio Fm. is observed near Amelia. This is an *unicum* in the whole UMS Domain and can be interpreted as the result of tectonic exhumation of a Jurassic margin of the Amelia PCP in the Early Cretaceous.

iv) the presence of mass-transport deposits (slumps and debris flows) in the uppermost part of the Maiolica Fm. and in the lower part of the Marne a Fucoidi Fm. is interpreted as due to the rejuvenated topographic gradient induced by faulting.

## A "middle" Barremian age for synsedimentary tectonics is indicated by the nannofossil assemblage of Maiolica-type facies sampled from the Mt. Cosce Breccia and from the neptunian dykes.

#### Biostratigraphic and Sr-isotope constraints on the Miocene transgressive surface in the Southern Apennines

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Keywords: Biostratigraphy, Sr-isotopes, Foraminifera.

In the Italian geological map, the Lower Miocene carbonate platform deposits cropping out along the Southern Apennines have been defined under several local names. Depending on the geographic position of the type area, they have been called as Cerchiara fm (North Calabria); Roccadaspide fm (Cilento area); Cusano fm (Matese area); Calacareniti di Recommone fm (Sorrento Peninsula). Notwithstanding differences in naming, grains composition is mostly uniform, while the genesis reflects a common tectonic context.

The Miocene carbonates get an outstanding geodynamic value because their emplacement seal the Apennine forebulge unconformity, marking the base of the foreland basin megasequence. Timing of carbonate emplacement tracks thus the migration of the forebulge. The top of Cretaceous or Paleogene carbonates involved in the peripheral flexuration represent the first transgression surface and the bedrock of Miocene carbonates.

In order to evaluate the timing of the forebulge migration in Southern Apennines, we carried out a detailed biostratigraphic analysis of the very first Miocene carbonates and that of the latest Cretaceous deposits just below the transgressive surface. The work comprehend four localities representing key areas of each formation name in Southern Apennine. We use larger Foraminifera as time markers for both Mesozoic and Miocene rocks supported by Sr-isotope analysis performed on pristine preserved bivalve shells, applied in order to solve discrepancies in the accuracy of larger Foraminifera biostratigraphy.

According Sr-isotopes and the presence of *Miogypsina globulina*, the first Miocene carbonates in North Calabria are upper Aquitanian in age. In Cilento area, oligotipic assemblage dominated by *Miogypsina globulina* suggests an Aquitanian age. After Sr-isotopes, the Miocene transgression in the Matese area began during middle Burdigalian. Here, two assemblages in two different outcrops (1) *Accordiella conica* plus *Rotalispira scarsellai* and (2) *Sabaudia capitata* plus conical agglutinated Foraminifera assign the age of the base to the Coniacian and Aptian respectively. In Sorrento peninsula, the Santonian-Campanian substrate with *Scandonea mediterranea, Dicyclina schlumbergeri* and *Rotalispira maxima* is overlain by middle-upper Aquitanian carbonates with *Nephrolepidina* and *Miogypsina*. Results show a time dependence of the Miocene transgression across the forebulge unconformity resulting in an eastward youngering of the carbonate system. The first Miocene deposits in Southern Apennine contain some rotaliids Foraminifera closely related to the r-strategist trophic-resistant *Ammonia* and *Rotorbinella*. This highlight the presence of run off with consequent delivery of fresh water and organic matter-rich sediments towards marine environments during the first phases of the lower Miocene transgression.

### Structural and stratigraphic reconstruction of an offshore portion of the sicilian hyblean foreland ramp

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Keywords: seismic stratigraphy, structural characterization, stratigraphic setting.

Based on the seismo-stratigraphic interpretation of new seismic profiles (Sparker System) acquired along the southeastern offshore of Sicily, this work contributes to the improvement of our knowledge about the stratigraphic and structural context in the area connecting the Gela-Catania foredeep to the Hyblean plateau foreland. Three main aims have motivated the acquisition of new seismic profiles along the southeastern coastline of the Sicily, in the Marina di Ragusa offshore: i) a better comprehension of the Cenozoic stratigraphic and structural setting of the area and, in particular, the characterization of the Plio-Pleistocene sedimentary deposits and their areal distribution; ii) the identification of the eventual continuation, in the offshore area, of the main structural lineaments defined in the hinterland (Scicli-Ragusa-Irminio line); iii) the understanding of the meaning of these faults on the geodynamic evolution of the Sicily Channel. A simplified model of the stratigraphic-structural setting of the study area is proposed with a comparison with preexisting models derived from the literature. Our model shows that an extensional faults system, characterized by a main NE-SW orientation, affects exclusively the late Miocene formation originating a horsts and graben setting. These faults are probably the record of the early history of the Scicli Line and of the polyphase kinematic evolution of the N50 oriented regional fault systems, supporting recent interpretations that identify an offshore prolongation of the NE-SW oriented faults of the Marina di Ragusa Graben. The Gessoso-Solfifera formation (late Miocene) has been recognized in several parts of the study area. It displays large lateral variation in thickness and a typical vertical arrangement of seismic facies showing that variable depositional environment characterized the Messinian salinity crise. Furthermore, internal erosional surfaces reveal that the deposition was not continuous in time but was associated with erosional periods that resulted in channelized features. More in general, the Gessosa-Solfifera deposits of the study area have a wide regional implication, demonstrating that the evaporitic deposits are not, as widely recognized on land, a peculiarity of marginal sub-basins or of the thrust top mini-basins of the Appennine-Maghrebides belt, but they also formed in the extensional setting of the Hyblean foreland ramp. Moreover, the acoustic features of the Plio-Pleistocene deposits have permitted the identification of six seismic units that correlate with the depositional evolution of the nearby Gela foredeep and with three formations with regional distribution: Trubi, Ponte Dirillo and Argo Formations. The Plio-Pleistocene succession is not affected by any tectonic activity, and consists of laterally continuous seismic facies, interrupted only in a wide area, where gas rising from the deeper succession reaches, in some places, also the seafloor

#### U-Pb detrital zircon ages from Gorgoglione Flysch sandstones (Southern Apennines, Italy): inferences on source area

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Keywords: detrital zircon age, source area, sandstones.

LA-ICP-MS U-Pb ages were collected on detrital zircons from one sample of sandstone belonging to the Gorgoglione Flysch (GF) outcropping in Southern Apennines (Basilicata Region, Italy).

The Gorgoglione Flysch represents a sedimentary siliciclastic succession having  $\approx 1500$  m thickness consisting of coarse-medium grained turbidites with mudstone layers. The deposition age of detritus was Langhian-Serravallian in a wedge-top basin belonging to the Southern Apennine Foreland Basin System (e.g. Lentini et al., 2002). GF sandstones show immature mineralogical composition and textural features. The composition varies from arkoses to lithic arkoses with some abundance of micas; the texture shows widespread siliciclastic and calcareous matrix and scarce cementation.

The provenance studies on GF sandstones based on quantitative modal analysis, indicated a crystalline basement formed by continental crust rocks located in the eastern sectors of the Alpine Chain (Critelli & Loiacono, 1988). The prevalent granitoids and low grade metamorphic rocks occur in the crystalline basement as testified by nature of lithic fragments in GF sandstones.

The detrital zircon radiometric dating through U-Pb spot analyses, tend to establish the ages of the source rocks supplying the sedimentation basin in Langhian-Serravallian times.

The age data collected on nine detrital zircons selected by one sample of sandstone reveal twelve ages ranging from Neoproterozoic to Triassic ages and four Oligocene-Aquitanian ages. The oldest age ( $669\pm25$  Ma) was measured on homogeneous luminescent zircon probably derived from metamorphites; a meaningful Carboniferous-Permian age cluster (n=10) ranging from  $319\pm13$  Ma to  $262\pm4$  Ma seem connected to zircons showing oscillatory magmatic zoning linked to granitoid and to recrystallized zircons in metamorphic conditions; one Triassic age ( $247\pm6$  Ma) was measured on broken crystal whereas four sub-concordant ages ( $25\pm1$  Ma to  $23\pm9$  Ma) are shown by two euhedral zircon crystals with regular oscillatory magmatic zoning.

The preliminary dating of detrital zircons from GF sandstones seem to indicate a provenance of detritus from Hercynian magmatic and metamorphic rocks forming the Alpine chain but the presence of a younger magmatic component suggested that even igneous rocks connected to Oligocene magmatic activity were present in the source area.

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### The Tell-Rif orogenic system (Morocco, Algeria, Tunisia) and the complex heritage of the southern Tethys margin

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Keywords: Tell, Rif, North Africa.

The Tell-Rif (Tell in Algeria and Tunisia; Rif in Morocco) is the orogenic system fringing to the south the West Mediterranean basins. This system comprises three major tectonic-paleogeographic zones from north to south: (1) the internal zones (AlKaPeCa for Alboran, Kabylies, Peloritan, Calabria) originating from the former northern European margin of the Maghrebian Tethys, (2) the "Flyschs zone" regarded as the former cover of the oceanic domain and (3) the external zones, forming the former southern Maghrebian Tethys margin. In the geodynamic frame of the West Mediterranean, the Tell-Rif is interpreted as the direct result of the progressive closure of the Maghrebian Tethys until the collision between AlKaPeCa and Africa and, subsequently, the propagation of the deformation within Africa. This gives a consistent explanation for the offshore Neogene geodynamics and most authors share this simple scenario. Nevertheless, the current geodynamic models do not completely integrate the Tell-Rif geology, in particular its non-cylindrical nature resulting from both the Mesozoic inheritance and the conditions of the tectonic inversion. During the Early-Middle Jurassic, we emphasize the development of NE-SW basins preceding the establishment of an E-W transform corridor connecting the Central Atlantic Ocean with the Ligurian Tethys. The Maghrebian Tethys developed just after, as the result of the Late Jurassic-Early Cretaceous left-lateral spreading between Africa and Iberia. By the Late Cretaceous, the occurrence of several tectonic events is related to the progressive convergence of the Africa and Eurasia. A major pre-Oligocene (pre-35 Ma) compressional event is recorded in the Tell-Rif system. The existence of HP-LT metamorphic rocks associated with fragments of ophiolites in the External Metamorphic Massifs of the Eastern Rif and Western Tell shows that, at that time, the western part of the North-African margin was involved in a subduction below a deep basin, element of the Maghrebian Tethys. At the same time, the closure of the West Ligurian Tethys through east-verging subduction led to a shift of the subduction, which jumped to the other side of AlKaPeCa involving both East Ligurian and Maghrebian Tethys. Slab rollback led to the development of back-arc basins (the Oligo-Miocene west-Mediterranean basins) on the site of the previous West Ligurian Tethys suture. The docking of AlKaPeCa against Africa occurred during the Late Burdigalian (17 Ma). Subsequently, the slab tearing triggered westward and eastward lateral movements at the origin of the Gibraltar and Tyrrhenian Arcs respectively. The exhumation of the External Metamorphic Massifs occurred through tectonic underplating during the westward translation of the Alboran Domain. It resulted in the formation of both foredeep and wedge-top basins younger and younger westward. The lack of these elements in the eastern part of the systems signs a different evolution dominated by frontal accretion.

### Tectonics as a key control on sedimentary processes and basin infill from the coastal areas to the deep-sea: examples from the Cefalù Basin (Northern Sicilian Margin, Southern Tyrrhenian Sea)

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Keywords: submarine canyons, turbidite depsoits, syntectonic deposition.

Tectonic processes are amongst the main controls on the creation and infill and on the stratigraphy, at a broad range of scales, both temporal and spatial, of sedimentary basins. They influence the grain-size and the amount of sediment fed into the basin, the extent of the continental shelf sediment staging areas, the connection between the coast and the canyon heads, the partitioning of sediment between the shallow- and the deep-sea, the development of geomorphic elements and facies, and depocenter location and shape. Tectonic activity has variable effects on sedimentation in the different depositional environments of a basin. In this paper, we present concepts derived from the recent depositional evolution of the Cefalù basin, with the aim of highlighting different aspects of the relationships between sedimentation and tectonics. The Cefalù Basin is a Pery-Tyrrhenian basin along the seismogenic northern Sicilian margin, and earthquakes can be at the origin of the numerous sediment failure scarps and mass-transport deposits, some of basin-wide extent. The width and the dip of the continental shelf result from tectonic activity along the coastal- and shallow-water areas and impact on the character of shelf deposition during the last sea level cycle. Furthermore, controlling the connection between the submarine canyons and the coastal areas, the width of the continental shelf determines the facies of the present-day high-stand deposits in the deep-sea fans of the basin plain. In the slope, active faulting governs the location of some of the sediment collapse areas and the character of some the channels. Beside resulting in linear channel courses, extensional faults impose to the channels an highly asymmetric profile: in the highest levee, in the footwall of the fault, sediment instability processes predominate; in the lowest levee, in the fault hangingwall, crevasse splay processes are eased. One of the slope channels cuts diagonally the slope, forced by the gradient created by the activity of the main extensional fault system that bounds the basin to the west. In the basin plain, the tectonic tilting causes the westward deflection of the frontal splay distributary channels and of the lobes. It also constraints the location of the basin plain main depocentre at the base of the faulted western basin margin that is steep and favour mass transport deposits intercalating with the otherwise turbiditic basin infill. Smaller faults control the distribution of intrabasinal depocenters and the facies and thickness of the single turbidite deposits. The faults, and the differential compaction acting in the various fault-block, fix depocentre position through time and do not permit allocyclic lobe deposit shifting. Our results serve as an illustration of the broad range of effects that tectonics has on the facies and stratigraphic architecture, at various temporal and spatial scales, and in different depositional environments, of a sedimentary basin infill.

#### Sedimentological features of a preserved Early Jurassic basin margin

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Keywords: Rift basin, basin margin, Jurassic.

The southwestern boundary of the Longobucco Basin (Northern Calabria, Italy), with a lateral continuity in excess of 20km, was surveyed in order to reconstruct the tectono-sedimentary evolution of the study area and to elucidate the nature of the contact between the Hercynian basement and the Mesozoic sedimentary cover. This had previously been interpreted as a thrust contact. The Sinemurian/Pliensbachian Fosso Petrone Fm., which is made of hemipelagic marls in the basin, is replaced by a chaotic clastic wedge in proximity of the basement, with clasts of the pre-rift units. The gravitative collapses driving the production of the breccia were triggered by an extensional tectonic phase, which produced submarine outcrops of the pre-faulting substrate (otherwise deeply buried in the basin depocenter) along fault escarpments, whose toe hosted the clastic body. Additional evidence of this tectonic phase are neptunian dykes crosscutting the basement and sealed by the same clastic body. Margin-collapse breccias are also found perched in morphological "bowls" carved along the escarpment profile, capped by thin condensed pelagites. Similar thin micrites drape locally also the metamorphites. The recovery of such pure pelagites ("epi-breccia" and "epi-escarpment" deposits, respectively) in a siliciclastic basin is accounted for by sedimentations in loci elevated with respect to the basin bottom, prior to their burial by the aggrading basin-fill succession. After the first tectonic phase, a period of marked subsidence was accompanied by the deposition of very thick turbidites (Trionto Fm.) and growth of an ephemeral shallow water carbonate factory (Lower Caloveto Fm.-LCF) attached to the unroofed footwallblock basement to form a fringing carbonate body.

The drowning of LCF in the latest Pliensbachian is constrained by the recovery of *Emaciaticeras* spp. in the turbidites onlapping and burying the LCF. This onlap indicates sinking of the fringing carbonates into deep water. A second generation of neptunian dykes cuts the basement and the LCF suggesting a further extensional phase. The geometries and contacts described above were preserved as the earlier faults were not re-utilized, the new ones being probably located "landward" or forming an angle with respect to the former.

In summary, the southwestern NW-SE trending present-day boundary of the Longobucco basin is interpreted as an Early Jurassic rift-basin margin, albeit locally overprinted by Tertiary thrusting, with well preserved stratigraphic contacts. The lower Sinemurian/Pliensbachian-lower Toarcian basin-fill units onlapped the Paleozoic basement via a discontinuous, narrow fringe of interposed shallow-water carbonates (Pliensbachian *p.p.*). Drowning of these small carbonate factories was caused by sinking into deep water in latest Pliensbachian time, a product of subsidence of the Calabrian continental margin.

### The role played by varying trophic conditions within the same rift basin in the development of carbonate bodies fringing different footwall blocks: the Lower Caloveto Fm. (Longobucco Basin - Sila Greca, Calabria)

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Keywords: Pliensbachian, platforms, trophic conditions.

Tethyan Pliensbachian carbonate platforms share many features in terms of biota, like the presence of a Lithiotis fauna, green algae and benthic forams associations. A carbonate platform is influenced, among other factors, by its position within a sedimentary basin, the inherited substrate, and the local trophic conditions. The carbonate factories of the Lower Caloveto Fm. (LCF- Early Pliensbachian/earliest Toarcian) differ from other coeval Tethyan platforms in terms of biota and depositional architecture, and are here discussed as case studies to investigate the control exerted by the abovementioned factors on their development.

The LCF grew on footwall blocks of the Longobucco rift basin (Sila Greca, Calabria): in the Longobucco area the benthic factory colonized a basin margin longer than 20 km, while at Caloveto it encircled a structural high. The LCF colonized the steep faulted flanks of the Hercynian basement, forming a very narrow belt of fringing carbonate bodies, up to 100 m-thick. The LCF is generally a lime grain- to floatstone with abundant sand- to pebble-size siliciclastic grains, indicating dominant high-energy conditions. Skeletal grains include crinoids, echinoids, bivalves, gastropods, Tubiphytes, benthic forams and calcareous sponges (Chaetetids). Non-skeletal grains include cortoids, peloids, and rare ooids.

The absence of green algae (e.g. Palaeodasycladus) as well as of aLithiotis fauna is linked with the geometry of the LCF, since these two organisms thrived in sheltered lagoons with muddy substrates, a depositional setting that did not exist in the peculiar sedimentary environment of the LCF, due to the very steep local substrate. For the same reason, large complex benthic forams like Orbitopsella, having an epiphytic mode of life, are also missing.

Differences exist also between the two study areas: 1) at Caloveto sub-reefal environments are recorded; at Longobucco, in contrast, highly integrated colonies are missing, and corals in general are rare; 2) at Longobucco red microbial crusts are common. These differences were probably due to the variable trophic conditions and sedimentary environments across the Longobucco basin. At Longobucco the development of coral reefs was likely prevented by eutrophic conditions due to organic matter supply from an attached mainland.

The Caloveto area, by contrast, was not backed by any vegetated continental area hosting a drainage system, as it constituted instead an Early Jurassic archipelago or isthmus distant enough from any source of organic matter to allow coral proliferation. In this light, the common microbialites at Bocchigliero/Longobucco would be linked with nutrient-rich waters, which is also confirmed by the dominance of low-diversity small-sized opportunist foraminiferal associations, typical of nutrient-rich environments, in contrast to the larger/complex forms which are completely missing as their endosymbionts require oligotrophic conditions.

#### Evidence of the Zanclean megaflood in the eastern Mediterranean Basin

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Keywords: Messinian Salinity Crisis, Megaflood, Evaporites.

The Messinian salinity crisis (MSC), regarded as an outstanding palaeo-oceanographic event that affected the Mediterranean region from 5.97 to 5.33 Ma (Roveri et al. 2014), was caused by a temporary restriction of the Atlantic-Mediterranean seaway that induced an imbalance between evaporation and water inputs (Flecker et al. 2015), transforming the Mediterranean Sea into a giant hypersaline lake and resulting in the deposition of kilometre-thick sequences of salts (the Mediterranean Salt Giant).

A widespread interpretation invokes the partial desiccation of the Mediterranean Sea during the Messinian (Hsü et al., 1973), with proposed sea level drawdowns of 1200-2700 m (Ryan, 2009; Urgeles et al., 2011), which requires the understanding of the mechanism that restored normal marine conditions at the end of the MSC.

Here we use geological and geophysical data to identify a buried wedge-shaped, chaotic sedimentary bodyup to 860 m thick and 1620 km<sup>3</sup> in volume - deposited in the western Ionian Basin after the massive Messinian salts and before the Plio-Quaternary open-marine sedimentary sequence. We show that this body is consistent with the passage of a flood from the western to the eastern Mediterranean Sea via a gateway today located in south-eastern Sicily. The depocentre of this body is located at the base of Noto submarine canyon on the eastern Sicilian margin, which bears a unique amphitheatre morphology comparable to more recent, welldocumented megaflood erosional landforms.

Our results provide support for the Zanclean flood as a Mediterranean-wide event. They can be used to improve the model of Zanclean flood dynamics in the Eastern Mediterranean Basin, infer dimensions of the gateway between the Western and Eastern Mediterranean Basins, and shed light on the sea level conditions and tectonic organisation of the central Mediterranean at the end of the MSC (Micallef et al., 2018).

The chaotic sedimentary body identified in the western Ionian Sea is the largest megaflood deposit on the planet in comparison to largest terrestrial events (Missoula, Bonneville, and Altay).

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### First results on the characterization of Capo D'Orlando Flysch (Calabria-Peloritani Orogen) through the integration of geomechanics and sedimentology

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Keywords: Flysch, Rock mass survey, Facies Association.

Heterogeneous rock masses, such as flysch formations, are characterized by a complex mechanical behavior, arising from either genetic or diagenetic phenomena. Dealing with flysch means dealing with a great variety of variables, including tectonic deformation and weathering processes, which lead to anisotropy in strength and stiffness of the outcrops. For this reason, their characterization needs an integrated study of geomechanics and sedimentology. In this perspective, this study reports on the sedimentological and mechanical analysis of the Capo d'Orlando Flysch (COF) to establish a methodological approach for a complete characterization. COF is a siliciclastic succession widely cropping out in the Peloritani Mountains, the southern termination of the Calabria-Peloritani Orogen in north-eastern Sicily. The current distribution of the flysch sequences is the result of an intense tectonic deformation associated to the activation of transcurrent faults systems, which affected the area since Tortonian. This tectonic regime is connected to the Africa-Europe collision and is responsible for the Tyrrhenian opening, along with the south-eastward migration of the Calabrian Arc. COF has been studied through the measurement of detailed sedimentological logs at two localities, Motta Camastra and Francavilla di Sicilia (north-eastern Sicily), where the formation offers some of the best exposed outcrops. In the studied sections, COF consists of a range of coarse- to fine-grained sedimentary facies, which can be grouped into three main facies associations: thick- to medium-bedded, amalgamated sandstones (F.A.1), medium- to thin-bedded sandstones and mudstones (F.A.2) and mud-prone deposits. In general, these deposits are interpreted as the product of high- and low-density turbidity currents and are consistent with a deepwater setting. Due to this heterogeneity, COF mechanical characterization was based on different approaches according to the recognized facies associations. In particular, rock mass surveys were carried out at F.A.1 sectors, where the outcrops can be assumed as sandstone rock masses affected by three or four discontinuity systems. On the other hand, where F.A.2 crops out, the alternation was considered according to the proportion between thickness of sandstone and mudstone levels. In this case, the geomechanical classification by Marinos and Hoek (2000), known as Geological Strength Index (GSI), allows the description of the lithology, structure and surface condition, with particular reference to the bedding planes. Achieved results demonstrate the utility of an integrated approach for the study of complex formations, where the mechanical classification cannot disregard the sedimentological setting.

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#### New indirect evidence of Permian bi-modal volcanism from sediment petrology in the Orobic Basin (Central Southern Alps, Italy)

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Keywords: Permian, Volcanism, Cabianca.

The Lower Permian Cabianca Volcanite (lower Collio Fm. *Auct.*), representing the filling of a large caldera, is dominantly acidic, as most coeval volcanics in the Southern Alps: intermediate rocks are rare and nearly irrelevant by volume (only two small andesite breccia pipes outcrop on the flanks of Mt. Cabianca). Subsurface data document the occurrence of an andesite body in the Novazza mine and a diatreme 2 km to the east (crossed by a prospection well), on the left Serio River valley. Out of the moat, Lower Permian pyroclastics outcrop along tens of kilometres, but intermediate rocks are unreported, except for the Val Pradini "porfirite amigdalare" in the west (Ornica). Permian volcanics and Variscan metamorphics are covered by Lower Permian sediments deposited in a transtensional basin, bound by steep faults and fringed by alluvial fans. The alluvial fan conglomerate of Val Sanguigno, north of Novazza, is dominated by andesitic clasts (cobbles-boulders), which reasonably derived from lavas that were outcropping beyond the southern boundary fault of the basin.

Investigations of the petrographic composition of the alluvial fan conglomerates carried out east and west of Mt. Cabianca, allowed comparing the composition of the volcanic rocks preserved in the depocentre (Cabianca Caldera) with the volcanic rocks cropping out outside of it, recorded in the clasts of the alluvial fans at the borders of the Orobic Basin. In the eastern (Lake Barbellino) and central (Val Sanguigno) parts of the basin, conglomerates at the southern border of the basin contain abundant intermediate pebbles, and an increasing proportion of basement clasts to the west. Conglomerates from the northern margin of the basin (Ponteranica Conglomerate, Pizzo dei Tre Signori massif) mainly contain pebbles and cobbles of metamorphic basement, acidic welded tuffs and, subordinately, of grey-green volcanics. In both cases, microscope analysis of associated litharenites revealed significant quantities of intermediate to basic volcanic lithic fragments. Visual estimates suggest that basic to intermediate clasts represent 15 to 20% of the bulk volume.

Petrographic composition of Lower Permian conglomerates confirms that Permian streams eroded both volcanic rocks and the Variscan basement, but documents that in the source area of the siliciclastics (i.e. highs bordering the basin) intermediate-basic volcanics were more abundant than in the Cabianca Volcanite. The relatively scarcer acidic pebbles in the conglomerate can be partly ascribed to the fact that they were still incoherent and reluctant to produce pebbles transportable over significant distance. Nevertheless, the high amount of basic-intermediate rocks documents that outside of the caldera these rocks were volumetrically abundant. This fact may be explained suggesting the existence of fractures and faults able to drive and trap basic-intermediate lavas documenting a clear bi-modal distribution of extrusives at the surface.

# The Late Tortonian-Quaternary kinematic model of central Sicily: new insights on the mode of deformation of the inverted African margin

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Keywords: Thrust and fold belt, Africa margin, Caltanissetta Trough.

The SE-verging Sicily thrust and fold belt, developed from the NW-SE oriented Nubia-Eurasia convergence, displays very impressive E-W trending tectonic lineaments, parallel to the convergent margin of the Western Mediterranean. We present the results of a detailed analysis of a vast area of central Sicily, including the Messinian Corvillo and Mandre thrust top basins, and the Plio-Pleistocene Centuripe basins. The study aims at the definition of the geometry and the kinematics of the E-W oriented tectonic features that control the northern margin of the Caltanissetta Trough and the recognition of their relation with the NE-SW trending lineaments of the thrust belt. The Caltanissetta Trough is a wide structural depression of the Africa lithosphere, which is infilled with the overriding allochthonous wedge, deriving from the closure of the Neo-Tethyan domain. Coherently with the plate motion, the E-W oriented shear zones show dextral displacements that superimposed on the NE-oriented features of the thrust belt. The analyzed dextral shear zones are part of a longer tectonic alignment, responsible for the lateral shifting of the major tectonic domain of the Africa margin, through the central Sicily. The surface interference pattern of central Sicily thus derives from the combination of dextral motion along wrench fault, rooted in the African margin, with the SE-verging thrust propagation due to the migration of the allochthonous tectonic wedge. In this tectonic context, the Early Messinian salt depocenters of the Corvillo and Mandre basins developed from tectonic collapses at the interference zone between two major wrench faults, while the Early Pliocene contractional deformation of the two basins is connected to motion within the allochthonous wedge. During the Late Pliocene and the Quaternary, the dextral shear zones propagated again across the allochthonous overburden to form the en-echelon features characterizing the Enna-Centuripe alignment.

According to the proposed model, the dextral shearing along the E-W oriented wrench faults could represent, since the Late Tortonian time, the surface expression of a permanent and dominant mode of deformation of the of the Africa lithosphere, involved along the western Mediterranean segment of the Nubia-Eurasia convergent margin. Thrust and fold belt, Africa margin, Caltanissetta Trough.

### New microfloristic data from the Rio Marina Formation (Elba Island): through a stratigraphic correlation of the Upper Palaeozoic successions in Southern Tuscany (Northern Apennines, Italy)

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Keywords: Permian, palynology, stratigraphy, Elba Island.

Recent stratigraphic studies on the Palaeozoic successions from Monticiano-Roccastrada Ridge (Southern Tuscany) provide the basis for original hypotheses on the significance of Tuscan Palaeozoic formations within the palaeogeographical framework of the western Mediterranean domain during post-Hercynian times. The present study is mainly focused on the first evidence of Permian sporomorphs in the metamorphic Rio Marina Formation exposed in the eastern sector of the Elba Island and their implications on the tectono-sedimentary history of the Tuscan basement, to which this unit pertains. The Rio Marina Formation mainly consists of alternations of graphitic dark-grey phyllites, metasiltstones and metasandstones with a maximum thickness of 250 m. Due to the scarce biomineralized content, the age of this formation was strongly debated in the geological literature, and alternately attributed to Carboniferous (Mississippian and/or Pennsylvanian), early Permian (Cisuralian) or middle Permian (Guadalupian) based on different correlations. Progress towards this goal has been achieved in this study with the finding of a quite well preserved and diversified microflora of Guadalupian age. Palynological assemblage shows analogous morphological characteristics with those documented in the metasiltites of Farma Formation, cropping out in the area of Monticiano-Roccastrada Ridge (Southern Tuscany). These close similarities allow to refer both formations as deposited in the same time interval and paleogeographic setting. Accordingly, these two formations could be considered a post-collisional deposit following the final consolidation of the Variscan orogen with associated deformation of related foredeep basins possibly in a relatively shallow-water marine setting.

#### Basins at convergent margins: evolution of the Messinian basins developed on top of the Sicilian Fold and Thrust belt

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Keywords: Messinian, Syntectonic Basin, Fold and Thrust Belt.

During the Messinian inherited palaeo-topography and ongoing deformation conditioned the depositional environments of the Mediterranean region, already strongly influenced by the effects of the salinity crisis. It occurred mainly in the central region, where seabed at that time is expected to be very uneven and shallower than Western and Eastern Mediterranean.

Indeed in this area as from 15 Ma the Sicilian Fold and Thrust Belt (SFTB) was originating, characterized by a multi-stage evolution. Two main shortening events generated and developed at different structural levels (shallow- and deep-seated thrusts following a thin-skinned thrust-model) and at different time intervals, involved mainly the Meso-Cenozoic carbonate units of the ancient African passive continental margin; a more recent thick-skinned thrusting involved the Plio-Pleistocene deposits in the frontal area, as well as the crystalline basement in the internal sector of the chain. Just in the Messinian time interval along the internal sectors of this edifice the transition from shallow to deep seated tectonics was recorded.

On top of the SFTB different types of basins originated progressively in response to the shortening wave. Depending on their position and related active processes during the Messinian we can distinguish: intramountain (mainly post-tectonic), thrust-top (syn-tectonic), and foreland (pre-tectonic) Messinian basins, with different characters and geometries.

Our results are only preliminary and could represent a first approach towards a better understand of the present complex distribution of the different variety of the Messinian sequences. The next step of this study should be the palinspastic restoration of the strongly deformed Messinian successions, in order to reconstruct a more detailed Mediterranean paleogeography.

# The tectonic and sedimentary framework of the Neogene-Quaternary back-arc and forearc areas, in the southern Calabria (south Italy)

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Keywords: Neogene-quaternary basins, Geodynamic evolution, Calabrian Terranes.

The tectonic and sedimentary framework of the Neogene-Quaternary back-arc and forearc areas, placed in the southern Calabria (south Italy), represent key sectors for understanding the structural and tectonostratigraphic evolution of the southern Calabrian Terranes during the Miocene-Recent time. Since the Miocene time, strike - slip, contractional and extensional tectonics influenced the Neogene-Ouaternary evolution of the back-arc and forearc domains in the southern Calabria (south Italy). The Calabrian Terranes (CT) is a narrow and arcuate subduction - rollback system related to the Africa/Eurasia plate convergence and the southeastward retreat of the Ionian slab. This generated a 10-30 km thick and 300 km wide subduction system, which includes a sub-aerial complex constituted by Paleozoic metasedimentary and plutonic rocks and Meso-Cenozoic sedimentary strata overlaid by a submarine accretionary wedge. From Middle Miocene on, the opening up of the Tyrrhenian back-arc basin produces a pulsating drifting of the Calabrian Terranes towards the south-eastThe migration of the Calabrian Terranes was drived by strike- and oblique slip fault systems, which produce the segmentation and partitioning of the orogen and the consequence formation of transversal and longitudinal basins. The southern Calabria is characterized by a forearc region, in the Ionian side, filled by 2000 m of Oligocene to Holocene sedimentary succession, and the related Tyrrhenian back-arc basin mainly characterized by Plio-Pleistocene successions and secondary miocenic successions. The sedimentary succession rests unconformably on crystalline metamorphic terranes of the southern Calabrian. The develop the Plio-Quaternary NE-SW fault systems and the NW-SE transversal fault systems further infuenced the evolution of the study area and its actual tectonic assemblage; these fault sistems are active, as evidenced by the seismic history and the instrumental recordings of Calabria.

#### Provenance evolution of the Julian Flysch Basin through geochronological and geochemical study of detrital zircon and rutile

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#### Keywords: Provenance, Zircon, Rutile.

The Julian Basin is located in the Julian Prealps (N-E of the Adria Plate) and it is a narrow, elongate basin, frequently tectonically active. Its southern border coincide with the carbonate Friuli Platform, which is the northwest extension of the Dinaric Platform. The age of deposition is Maastrichtian -Early Eocene. The mixed carbonate and siliciclastic deposits can exceed the 4000 m of thickness and are the result of a first Alpine tectonic phase, in which the sediment was brought from the North and a final turbiditic phase triggered by eustatic sea-level changes (Tunis & Uchman., 1996 and references therein).

The main heavy mineral phases constituting the sedimentary rocks are spinel, garnet, pyrite, zircon and rutile. The spinel fraction shows volcanic and peridotitic affinities, while the chemistry of the garnet suggests several protoliths (i.e. metapelites, granitoids and metamafic rocks) (Lenaz et al., 2000). Zircon ages and trace elements and rutile geochemistry is here used to better understand the evolution of the clastic sources of the Julian Flysch Basin through time and to give new insights on the supply area.

Magnetic and heavy liquid separation with Tetrabromohethane (2.97 g/cm<sup>3</sup>) have been applied on grains with a size between 63 and 250  $\mu$ m to isolate the non-magnetic heavy mineral fraction. Optical microscope, cathodoluminescence and Raman spectroscopy have been used for the mineralogical identification. Finally, LA-ICP-MS analyses have been performed for age determination and trace element geochemistry.

The first results indicate that, in the Julian Basin, zircon ages span between 180±3 and 3286±43 Ma while the trace elements suggest both magmatic and hydrothermal origin. The rutile chemistry points out their main crustal-metapelitic derivation.

#### Architecture, timing and triggering factors of the Crotone Megalandslide, southern Italy

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Keywords: Crotone Megalandslide, Calabria, Ioanian Sea.

A large-scale gravitational phenomenon off the Crotone Basin, a forearc basin located on the Ionian side of Calabria (southern Italy), is documented by seismic, morpho-bathymetric and well data, and by the analysis of land movements. This large landmass, referred to as the Crotone Megalandslide, extends for at least 500 km<sup>2</sup> and is ca. 1.5 km thick (Minelli et al., 2013; Zecchin et al., 2018). It started moving between Late Zanclean and Early Piacenzian and was triggered by a contractional tectonic event (Zecchin et al., 2015) leading to the basin inversion. Seaward gliding of the megalandslide continued until roughly Late Gelasian, and then resumed since Middle Pleistocene with a modest rate (Zecchin et al., 2018). Interestingly, the onshore part of the basin does not show a gravity-driven deformation comparable to that observed in the marine area, and this peculiar evidence allows some speculations on the origin of the megalandslide.

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### Seismostratigraphic reconstruction of the Messinian palaeotopography across the Northern Sicily Continental Margin (NSCM) and an overlying Zanclean megaflood deposit

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Keywords: Messinian paleo-topography, Zanclean flood, Mass Transport Deposits.

During the Messinian salinity crisis (MSC) (from 5.97 to 5.33 Ma), the Mediterranean Sea became disconnected from the world's oceans and a fast and continuous evaporation resulted in its partial desiccation. One of the theories for the end of the MSC postulates that a large volume of Atlantic waters entered the Mediterranean Sea through the Gibraltar Strait and rapidly refilled the Mediterranean basin in an event welldocumented known as the Zanclean Flood. The pathway of the Zanclean flood during its passage from the western to the eastern Mediterranean Sea is unclear. The aim of this study is to understand the effects of the Messinian palaeotopography of the southern Tyrrhenian Sea on the dynamics of the Zanclean flood. We analysed a large number of multichannel seismic reflection profiles acquired in the Northern Sicily Continental Margin (NSCM), calibrated with stratigraphic log from the Agip/ENI wells, and high-resolution multibeam data showing the present-day morphology. A detailed seismostratigraphic and structural analysis of these data allowed us to identify two different types of chaotic bodies in the Plio-Pleistocene sedimentary succession. The first type consists of a very thick deposit characterised by chaotic to transparent seismic facies, deposited nonconformingly above an older substrate with a very high-amplitude reflector along its top. This older substrate correlates to the MES horizon (Lofi et al. 2011). The second type consists of thinner bodies having smaller volumes and chaotic seismic facies interbedded with the well-stratified Pleistocene-Holocene deposits. We interpret the Pleistocene-Holocene chaotic bodies as small-scale mass transport deposits (MTDs) that are mainly located at the foot of steep escarpments and partly triggered by the compressional, extensional, and strike-slip Plio-Pleistocene tectonics. We hypothesise that the larger chaotic body is a flood deposit, possibly emplaced by a branch that separated from the main flow transferring water and sediment through the Sicily Channel (Micallef et al., 2018). Based on the reconstructed Messinian palaeotopography of the southern Tyrrhenian Sea, the Zanclean flood flowed from west to east across an elongated depression that is now bordered by the "Elimi Chain" to the north and the Sicilian coastline to the south. The material transferred was finally deposited at the toe of Scuso bank and Solunto high.

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## **Session S9**

# Faulting and folding across the scales. How, where, and why the lithosphere deforms

Conveners AND CHAIRPERSONS Fabrizio Balsamo (Università di Parma) Stefano Tavani (Università di Napoli-Federico II) Stefano Zanchetta (Università di Milano-Bicocca) Massimo Mattei (Università di Roma Tre)

### Deciphering the timing of deformation of polyphase crustal-scale faults in northern Iberia, Spain: Insights from K-Ar dating of clay gouges

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Keywords: K-Ar dating, polytype determination, northern Iberia.

The kinematics of faulting in the Iberian plate during the Mesozoic is a poorly known issue because the Mesozoic extensional activity of many structures is hindered by inversion tectonics during the Cenozoic or by renewed extensional activity during the Oligocene and Miocene linked to the evolution of the eastern margin of Iberia and the opening of the Valencia Trough.

Nine samples from clay gouges of inferred Paleozoic to Paleogene age from two major crustal-scale faults in northern Iberia (Vallès-Penedès and Río Grío Faults) were separated into 44 grain-size fractions (6-10, 2-6, 0.4-2, 0.1-0.4 and <0.1  $\mu$ m), analyzed by X-ray diffraction in order to determine the mineralogical assemblages and mineral variation within each fraction and dated by K-Ar.

K-bearing minerals are mainly K-white mica/illite and subordinately K-feldspar that does not exceed 3%. Polytype determination reveals that the 10Å-phase is a mixture of inherited and authigenic minerals for both faults characterized by illite/muscovite-2M<sub>1</sub> in the coarse fractions and by illite-1M and illite/muscovite-2M<sub>1</sub> in the finer fractions. Generally, a decrease of illite/muscovite-2M<sub>1</sub> content is balanced by the neoformation of illite-1M and smectite and/or mixed layers illite-smectite in the finer grain-size fractions indicating that the latter represent authigenic phases formed synkinematically during fault activity. Oriented ethylene-glycol solvated patterns for undeformed rocks and clay gouges from the Rio Grío Fault display long-range ordered (R3) I-S with similar illite contents suggesting that faulting occurred at depths (and temperature) similar to those recorded by the underformed rocks during shallow burial in late diagenetic conditions. Clay gouges of the Vallès-Penedès Fault display discrete illite/muscovite and paragonite pointing to higher deformation temperatures, possibly related to hot fluid circulation.

Each grain size fraction was dated by K-Ar analysis of synkinematic illite-muscovite depicting a polyphase tectonic activity for both faults since the late Permian. K-Ar ages show a significant grain size-dependent age variation. The age intervals documented correspond to well-known key episodes of the tectonothermal evolution of the Iberian Plate. An Illite Age Analysis (IAA) approach of the obtained K-Ar ages was necessary to statistically interpret the dates. The ages point to three main deformation events for the Vallès-Penedès and Río Grío Faults of: 1) Middle-Late Jurassic age, linked to the opening of the Central Atlantic Ocean; 2) Campanian-Maastrichtian age, linked to the end of rotation of Iberia with respect to Europe, and an overall change from transtensional to transpressional conditions; 3) Eocene age, related to Paleogene compression.

#### Lab-scale subduction megathrust earthquakes: applications and future directions

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Keywords: subduction megathrust earthquakes, analog modelling, interseismic coupling.

Subduction megathrust earthquakes are among the most dangerous geo-hazards. Stress build up caused by plates convergence and friction acting along the megathrust is episodically released by ruptures that may span several hundreds of km, resulting in magnitude 8 or larger earthquakes. The short instrumental record and the multi-scale, multi-parameter influence complicate our understanding of the origin and loci where those earthquakes may occur in the future. These two types of complications are perfect targets for analog modeling. This technique in fact allows reproducing a given geologic process in space- and time continuum and in convenient temporal- and spatial scales. Moreover, analog models allow testing various parameters influence simply changing the boundary conditions.

Here, I use a new laboratory model featuring a flat subducting plate driven at constant velocity and underthrusting a viscoelastic gelatin wedge (analog of the overriding plate) to mimic several seismic cycles. In the model, stress build up is episodically released via spontaneous ruptures that propagate along the analog megathrust. The rupture width-slip proportionality and seismic moment-duration scaling have been investigated aiming to test dynamic similarities with natural earthquakes. I use this model to investigate the asperities synchronization process and the relevance of interseismic coupling maps for inferring the pattern of future earthquakes. Experiments show that the barrier-to-asperities length ratio Db/Da plays a relevant role for the synchronization process. In particular, a permanent barrier is observed for Db/Da > 0.5 and an inverse proportionality between Db/Da and the percentage of events with synchronized asperities rupture is observed when Db/Da < 0.5 Regarding the correlation between interseismic coupling maps and slip distribution, experiments suggest that interseismic coupling has a low predictive potential for constraining the lateral extent and, in turn, the magnitude of future earthquakes. The area of maximum of slip, on the other hand, display a strong correlation with locked regions.

I will conclude showing that the lab-scale mega-earthquake model can be used for testing the performances of Machine Learning algorithms. Preliminary investigations reveal that long timeseries of dense geodetic-like information will help to shed new light for predicting the pattern of future earthquakes.

### New data of Catania Anticline activity in the western area of Misterbianco Town (eastern Sicily)

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Keywords: Tectonics, Catania, active folding.

In the last decades several geological morphological and morphotectonic analysis accompanied by geodetic and geophysical survey have highlighted occurrence of a huge WSW-ENE trending active anticline, named "Catania Anticline", in western sector of Catania Town until Misterbianco eastern neighbors. This structure is coupled with an active and comparable trending syncline connecting the Terreforti Anticline and Catania Anticline.

Recently, stratigraphic data from the Misterbianco "Zona Commerciale" revealed Stentinello aged pottery (5.5 ky b. C.) in the thin paleosoil interposed between Quartararo lavas (15-3.9 Kys) and overlying Holocenic alluvial deposits cropping out in the C.da Mezzocampo.

The folding activity, indeed must be backdated at most to 7500 b.p. and the deformation rate could be estimated in 5 mm/yr for the Catania Anticline whose growth of 40 m in his axis occurred in the last 7500 yrs. Therefore, the vertical deformation rate could be minor of previous estimates, whilst the inferred deformation of the C.da Mezzocampo syncline allowed to identify a maximum vertical deformation of the southern flank of the syncline not less than about 10 m.

In the present work we present new geological and morphostructural data carried out by recent field survey in C.da Vazzano-Erbe Bianche, in the far western sector of the Municipality of Misterbianco next to the M. Tiritì and Piano Tavola village area. This survey, performed as part of a public building project, highlighted recent deformations referable to Catania Anticline activity, extending in this area the occurrence of the active anticline previously confined in the eastern side of Misterbianco Town.

In particular we analyze the following topics:

a) the C.da Vazzano-Erbe Bianche area could be represent the periclinal termination of the Catania Anticline as evidenced by the alluvial deposits since we have measured a NNW dipping attitude from western suburbs of Misterbianco Town toward Piano Tavola Village, with total slope of about 10 m;

b) the Erbe Bianche area represent also a slight antiform culmination as termination of the anticlinal hinge;

c) In the lower slope of M.Tiritì alluvial deposits show NNW-SSW trending morphostructural flexure characterized by variable difference elevation of about 2-4 m and we suggest that this morphostructure could be interpreted as recent faulting connected to the M.Tiritì system fault already showed in literature.

Finally, in the Misterbianco Town, the Catania Anticline axis is marked by several aligned "tumuli" mostly exhibiting contractional structures in the core and extensional joints at top.

In conclusion, the western side of the Catania Anticline is well represented by clear field data demonstrating active folding and faulting of the Catania Anticline activity.

### Calcite-cement precipitation mediated by cataclastic shear bands in arkosic sand: petrophysical and mechanical considerations

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Keywords: Arkosic sand, Cataclastic shear bands, Calcite nodules.

Porous sandstones are important reservoirs for geofluids. In this kind of granular materials, the interplay between deformation localization and cementation is critical since both processes can strongly reduce rock permeability thus, baffling the fluid flow. We study cataclastic shear bands (CSB), in a high-porosity sandstone unit (Loiano Fm. - LS) exposed in the Northern Apennines that presents a spatially heterogeneous carbonate cementation. The Middle Eocene LS are proximal turbidite deposits of poorly consolidated and immature sandstones. CSB localize carbonate diagenetic structures in the form of isolated spheroidal or irregular-shape nodules and tabular concretions evident thanks to differential erodibility respect to the poorly cemented host rock (Hr). The primary research questions that we address in this work are: (1) How did the CSB localize the cementation? (2) How did the CSB and cementation affect the Hr in terms of petrophysical and mechanical properties? Answering these questions is critical to assess the relationships among structures, cementation, and fluid flow. Combining optical and electron microscope analysis with digital image processing, we assessed that the LS are medium-grained and mostly made-up by Quartz (Qz: 49-60%) and Feldspars (Fsp: 39-48%) with a few rock fragments and minor accessory. Manual point counting validated this composition. Thus, LS can be classified as an arkose. Hr total 2D optical porosity is between 20 and 24%; in the cement nodules, total porosity is 0.70-1.30% and skeleton porosity is 20-23%. Grain size and porosity reduction start affecting Hr porosity approaching the CSB. The skeleton porosity reduces to 4-8% in the CSB. The Fsp grains within the CSB show a grain-size reduction mainly by intragranular fracturing preferentially oriented along cleavage planes. Qz grains, on the other hand, do not show any preferential fracture direction. Thus, Fsp grains tend to preserve/increase their aspect ratio (roundness shows opposite trend) in the CSB. Fsp grains contribution to the increase in fine grains content within the CSB prevails, although the Hr grain size distribution is similar for Qz and Fsp. Analysis of grain angle in the CSB, shows that some grains, mostly Fsp, tend to align with the shear direction. Rock compressive strength [MPa] evaluated with the Schmidt hammer shows higher value for cement nodules [61] with respect to Hr without nodules [24]. This is mostly caused by cementation. The cataclasis in the CSB affects flow and may have been critical in focusing cementation. Different scenarios are possible; we think, however, that the carbonate cement precipitation occurred where the fluid flow slows down (low permeability and advective velocity) and where a major grain surface area is available (fine grain-size). These two conditions occur in the CSB due to cataclasis development. CSBs, therefore, could be a place of preferential nucleation of the carbonate nodules as observed in the field.

# Backthrusts occurrence in fold-thrust belt and their effect on extensional fault displacement estimations: field evidence from the Middle Val Roveto, central Apennines, Italy

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Keywords: Pop-up structures, Backthrust, Fold-thrust belts.

We combined structural and stratigraphic methods to highlight the deep structure along the axial sector (Middle Val Roveto) of the central Apennines fold-thrust belt, where no seismic reflection profiles or boreholes are available, despite the occurrence of major thrust fronts (i.e., the Simbruini-Ernici and Vallelonga thrust fronts) and one of the longest seismogenic extensional faults of the Apennines (i.e., the Val Roveto Fault). The Middle Val Roveto has a tectonic origin, being bordered on its southwest margin by the SW-dipping and NE-verging Simbruini-Ernici thrust front and on its northwest margin by the SW-dipping Val Roveto seismically-active extensional fault. In particular, previous studies indicated that the Val Roveto extensional fault cuts a NE-dipping monocline (i.e. the Mt. Cornacchia ridge), consisting of >3 km-thick Meso-Cenozoic carbonate platform deposits.

However, in this work we present new field data and structural analyses, which reveal a complex geologicalstructural setting along the northeast margin of the Middle Val Roveto. In particular, we document the occurrence of SW-verging overturned anticline and associated syncline. This evidence suggests the occurrence of a buried backthrust at the base of the anticline. Both the anticline and syncline are cut by the Val Roveto extensional fault, which clearly postdate the compressional deformation. In particular, we suggest that the inferred backthrust is coupled with the Vallelonga thrust front, showing a typical Apenninic vergence (i.e., towards the northeast), which is exposed along the northeast margin of the Mt. Cornacchia ridge. Therefore, we interpret the backthrust-frontal thrust system as a double-verging pop-up structure produced during the compressional phase of central Apennines fold-thrust belt accretion.

We conclude that the possible occurrence of other buried (i.e., as located in the hangingwall of seismogenic extensional faults) backthrusts and associated pop-up structures in the central Apennines can generate overestimations of seismically-active extensional fault displacements.

#### Paleo-depth of fault activity: an estimate from paleostress state calculations

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Keywords: fault-slip data, paleostress, fault depth.

Paleostress state reconstructions using fault-slip data yield the orientation of principal stress axes ( $\sigma 1 > \sigma 2$  >  $\sigma 3$ ) and the ratio of the difference between principal stress magnitudes, i.e. the reduced stress tensors.

To reconstruct the complete stress tensor (defined by six independent variables), we need to determine the two remaining unknowns, using the rupture and friction laws (Angelier, 1989).

With the complete stress tensor and some constraints on the pore pressure, we can infer a depth interval of fault activity.

The method we propose is organized into different steps:

- 1. collect fault slip data;
- 2. calculate the reduced stress tensor through inversion of fault-slip data; we used the FSA software (Célérier, 1999);
- 3. calculate the complete stress tensor using: 3a) the friction law and 3b) the rupture law.

3a. The initial friction law is considered linear and intersecting the origin. All inherited faults, reactivated under the investigated stress field, correspond to points in the Mohr space that should lie on or above the initial friction line and below the failure envelope. As a consequence, defining the lower boundary of the cloud of points, we can identify the friction line. This operation fixes the abscissa origin of the Mohr diagram.

3b. We chose the rupture law of Hoek & Brown (1980) and calculated it with the software RocLab<sup>®</sup>:  $\sigma'_1 = \sigma'_3 + \sigma_{ci} (m \sigma'_3 / \sigma_{ci} + s)^{0.5}$ , where  $\sigma'_1$  and  $\sigma'_3$  are the major and minor effective principal stresses at failure;  $\sigma_{ci}$  is the uniaxial compressive strength of the intact rock material and m and s are material constants.

Moreover, in our fault population, we identified couples of conjugate faults, which are neoformed by definition. The angle between these faults ( $2\Theta$  angle) fixes a point on the largest Mohr cicle, where the rupture law has to be tangent. This defines the scale of the axes, and therefore the values of the principal stresses;

4. Define paleodepth.

Provided that one of the principal stresses is close to vertical, it will represent the vertical stress (s<sub>v</sub>) and therefore the lithostatic load. Assuming the average density of overlying rocks and the hydraulic conditions (i.e. the amount of pore pressure, P<sub>f</sub>) we can then calculate paleo-depth, considering that:  $\sigma_v = \rho gz$ , with  $\rho =$  density of the overburden, g = acceleration gravity (9,81 m/s<sup>2</sup>), z = depth, and  $\sigma'_v = \sigma_v - P_f$ , where  $\sigma'_v$  is the effective vertical stress.

We report here our preliminary test in a well-constrained geological occurrence, and show that the calculated depth of fault activity fits well the depth derived from independent, stratigraphic investigations.

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# Diagenetic evolution of carbonate fault rocks associated to extensional normal faults of central and southern Apennines

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Keywords: Fault Core, Structural Diagenesis, Extensional Faults.

This work is aimed at assessing the time-space diagenetic evolution of carbonate fault rocks cropping out along extensional fault zones of central and southern Apennines, Italy. The goals is to decipher the interplay between brittle deformation and diagenesis of both calcite- and dolomite-rich carbonate fault rocks, which underwent to a quick exhumation from shallow crustal levels since Pliocene times. The structural diagenesis of carbonate fault rocks, which means the interaction between cataclasis and the physical-chemical changes due to diagenetic processes, is hence the topic addresses by the present contribution. The comprehension of the aforementioned interactions has become increasingly important due its wide range of applications, such as management and protection of geofluids,  $CO_2$  storage in the underground, production of geo-thermal energy, etc. In light of the reasons above, the study focuses on the follwong objectives: (i) assessment of the nature, distribution, and relative timing of formation of the calcite cements present within the fault rocks; (ii) decipher possible discrepancies between cements in limestone- and dolostone-hosted fault zones; (iii) inferences on the hydrogeological conditions at which cement precipitated in light of the existing stable isotope data of the study fault zones.

The study was performed on fault rock samples collected from 5 different extensional fault zones. crosscutting either dolosotones or limestones. One of them crosscut an alternation of limestoness and dolostones, and it is hence considered as a middle member among the all other study cases. After detailed field structural analysis and sample collection, X-ray diffraction of powder samples, optical microscopy, electronic scanning microscopy of oriented thin sections, and SEM-cathodoluminescence analyses of selected thin sections, the following results were achieved: (i) cementation was more pervasice and widespread within calcite-rich fault rocks than dolomite-rich ones, due the control exerted by the host rock in the availability of calcium carbonate along the fluid pathways in the subsurface; (ii) cement distribution within the fault cores is controlled by their internal architecture in relation to the paths of cementing fluids oversaturated in calcium carbonate; (iii) the calcite cements are diagnostic to assess environment of precipitation. In fact, deep-to-shallow phreatic and vadose conditions were deciphered for the study calcite cements. By taking the aforementioned result into account, and considering the existing literature, data are summarized in a general conceptual model tackling the structural diagenesis of carbonate fault rocks exhumed from shallow crustal levels.

#### Structural diagenesis of platform carbonates: role of possible early embrittlement on fracture development and distribution

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Keywords: Fractures, Apulian Carbonates, Diagenesis.

Diffuse fractures perpendicular to sedimentary beds are common features in carbonate rocks, in which several studies documented how distribution, dimension and overall geometry of the bed-perpendicular joints are affected by primary heterogeneities such as bed interfaces, erosional surfaces, transgressive surfaces, ecc. On the contrary, some others showed that early embrittlement caused development of vertically persistent, opening-mode fractures prior to formation of the aforementioned heterogeneities during diagenesis of platform-related carbonates. This means that filed analysis of both abutting and crosscutting relationships between primary (depositional and diagenetic) and secondary heterogeneities (due to deformation) might bring to misleading results if their relative timing of formation is not clearly documented. This study focuses on the structural, petrographic, mineralogical, and petrophysical analyses of Early Cretaceous limestones exposed at the Monte Alpi, southern Italy. The goal is to decipher how both geometry and distribution of bed-perpendicular mode-I fractures vary within individual limestone beds as function of their depositional environments and diagenetic evolution. Study limestone beds exposed at the Monte Alpi, southern Italy which are pertaining to the Inner Apulian Platform, and consist of a wide spectrum of calcareous facies made up of mudstones, wackestones, packstones, grainstones and microbial bindstones, which are related to a variety of depositional environments within a back-reef inner platform / platform margin of a rimmed platform (i.e., Apulian Carbonate Platform).

The aforementioned objective is achieved by conducting a multidisciplinary study at multiple scales of investigation, from outcrops to microscales. First, field stratigraphic analyses permit to unravel the composition of bed interfaces. Then, detailed meso-and micro-scales fracture analyses is key to document the abutting and crosscutting relationships between bed-perpendicular joints and both bed interfaces and bed-parallel stylolites present within individual beds. Finally, optical microscopy, SEM and cathodoluminescence analyses of samples collected form specific limestone beds allow inferences on their depositional setting and diagenetic history. P-wave velocity and porosity measurements performed on collected samples will shed lights into the petrophysical properties of the carbonate matrices pertaining to the study beds, and in particular will allow to unravel the pore type associated to the several analysed lithofacies. Integration of these results with those after structural diagenesis of the limestone beds petrophysical analysis will likely show how carbonate textures, depositional settings and diagenetic histories are keystone controls exerted on early embrittlement processes, on the storage and migration properties through the fractured limestone succession.

#### Control of the inherited structures on the Miocene orogenic evolution of the High Atlas (Morocco)

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Keywords: High Atlas, Exhumation.

The High Atlas of Morocco is an intracontinental mountain belt which reaches over 4000 meters of elevation. It is a double-vergen ridge developed during the Cenozoic by the inversion of Triassic-Jurassic rift structures and its evolution is tied to that of the Anti-Atlas, its southern foreland.

The High Atlas has remarkable variations in terms of width, elevation and cooling history along and across the strike. In order to understand the meaningful cause of this changing, in this work we present morphometric and thermochronological data and their relationships with the structural styles of deformation.

We present 35 new mean (U-Th-Sm)/He (AHe) and 24 new fission-track ages (AFT) on apatite from the High Atlas and from the Anti-Atlas. Our new AHe ages range from 141.1 Ma to 5.1 Ma and our new AFT ages range from 196.0 Ma to 10.4 Ma. The Miocene-to-Pliocene cooling ages are found in the axial region of the High Atlas whereas in the Anti-Atlas the youngest cooling age is Oligocene (33.8 Ma). In the High Atlas, our new data together with previously published results, constraint the amount of Cenozoic exhumation between > 4 km and < 6 km and the maximum exhumation rate in the range of 0.22 - 0.25 Km/Ma. In the Anti-Atlas, the maximum amount and rate of Cenozoic exhumation are  $\leq 2$ km and  $\approx 0.05$  Km/Ma, respectively. Close to the southern and northern bounds of the High Atlas belt, exhumation from a depth >1.9 km and <4 Km occurred in the Miocene along transpressive and thrust faults. In the High Atlas, the spatial patterns of the amount and rate of exhumation and of the topography are similar. In fact, exhumation peaks along the belt axes where the topography is higher, the belt is narrower and the steepness indexes of rivers are higher. Moreover, it decreases with the topography northward and southward towards the forelands, and westward and eastward as the belt becomes wider and as stratigraphically younger units are exposed at surface.

Since the rainfalls are low and the variations we observe along the High Atlas are sharps, we exclude the climate as main controlling factor to shape the topography. We suggest how the tectonic occurring in the upper crust is the first order process to control in the surface evolution of the High Atlas.

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#### A rheological transect across the Hellenides

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Keywords: Rheology, seismicity, Hellenides.

We realized several 1D rheological profiles along a transect crossing the Hellenides mountain belt and the northern Aegean Region, from the Ionian coast to eastern Macedonia, with the principal aim of analysing the depth of the brittle-ductile transition. Vertical yield strength envelopes have been laterally interpolated in order to distinguish the brittle from the ductile crustal layers and hence to define the BDT depth along the transect. At this regard, the depth of the BDT represents a crucial information for improving the seismotectonic parameterization of major active faults, since it approximately represents the bottom of the seismogenic layer (see e.g. Sibson, 1982). In particular, reducing its uncertainties, could help constraining the maximum potential width of crustal faults, whose termination at depth is often still debated. Pseudo 2D sections of the maximum rock strength, which represents the lateral variability at depth of the rock behaviour, and of the geothermal gradient, have been also tentatively reconstructed. In order to implement the 1D rheological modelling we used a purposedly developed Matlab code, where we iteratively compute the minimum strength between that associated to frictional sliding behaviour and the one related to the ductile power-law creep, at vertical steps of 100 m. As far as the investigated transect crosses very different geological, tectonic and geodynamic settings, going from continental collision (fold-and-thrust-belt environment), in the west, to crustal extension characterized by shallow normal faulting and metamorphic core complexes exhumation, in the east, the several input parameters (such as the heat flow, strain rate, tectonic regime, lithological layering, crustal structure, pore fluid pressure) have been carefully constrained on the basis of the available literature and geological/tectonic considerations. The influence of each parameter and of their combinations on the lateral changes occurring in the rheological properties, such as the BDT depths and strengths, have been also investigated showing that the heat flow, and to a lesser extent, the lithological stratification, are the main factors controlling the distribution at depth of the rheological characteristics of the crust across the Hellenides, and in particular of the BDT position. The preliminary results show that the BDT depth progressively increases from east to west reaching a maximum value in correspondence of the mountain chain axis.

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# Microstructural records of a polyphase hydrothermal fluid-rock interaction along exhumed faults in northern Victoria Land (Transantarctic Mountains, Antarctica)

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Keywords: Fluid-rock interaction, hydrothermal fluids, exhumed fault zone.

The tectonic history of northern Victoria Land (nVL), at the Pacific termination of the Transantarctic Mountains, is still partially unresolved. The present structural architecture of nVL is characterised by km-scale NW-SE striking lineaments, that transect the crust and the Ross Sea Cenozoic rift basins. The arrangement and amalgamation of different lithotectonic units have been related mainly to Cenozoic intraplate right-lateral shear, overprinting pristine structures that are linked to the Early Paleozoic Ross orogenic event in Antarctica; evidence for intervening tectonic events remain still unresolved.

Recent structural field work reported at least two tectonic increments of post-Ferrar late Mesozoic to Paleogene age, that are overprinted by the Cenozoic (mainly Neogene) dextral strike-slip event. This testifies that nVL consists of highly anisotropic crust which mainly formed during the Ross-orogenic event; moreover it is *a priori* highly susceptible to any repeated reactivation of inherited Paleozoic to Mesozoic tectonic discontinuities, after the initial break-up of Gondwana, coincident with the Ferrar Igneous event at ca. 180 Ma.

Here, we report regional-scale syntectonic hydrothermal alterations occurring along different exhumed fault systems in the Bowers Mountains and the Rennick Glacier area in nVL. The damage zones of these faults show pervasive syntectonic metasomatic recrystallization of the country rock, consisting mainly in: carbonation and silicification of gabbro and ultramafic rocks; Mg-Ca-Fe carbonation of metavolcanic rocks (accompanied by carbonate coatings on fault planes, hydraulic breccia, and quartz-carbonate veining) and epidotization (epidote, chlorite and prehnite) of gouge and cataclasite in granitoid rocks and in metabasalts. We focus on the preliminary study of one cm-thick detachment from a fault system in the Granite Harbour Intrusives; host granitoid is made mainly by K-feldspar, plagioclase, biotite and quartz (plus minor zircon and apatite). The mini-detachment is characterised by alternating green and dark-green mm-wide layers of cataclasite, ultracataclasite and pseudotachylite, with superposed slip zones and microfractures filled by prehnite. The magmatic minerals of the wall rock are partially replaced by saussurite, chlorite, epidote, prehnite and minor sphene. Microstructural and petrological investigations of this detachment zone provide important constraints not only for the understanding of the mechanical behavior of the fault and the complex fluid-rock interactions during deformation, but moreover it presents a first hint to unravel the polyphase tectonic history of this sector of the Transantarctic Mountains and the interaction among fault activity and volcanism during Gondwana break-up.

# Real and virtual outcrops to characterize the internal structure of a carbonate-hosted fault zone: the Tre Monti fault case study in Central Italy

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Keywords: fault structure, damage zone, carbonate-hosted fault.

A fault zone is composed of one or multiple fault cores, which are located within a complex network of fractures and secondary slip surfaces (i.e., the damage zone) that determine the mechanical behaviour. For example, fractures within the damage zone control fluid circulation and have a strong impact on the elastic properties of the host rock. Furthermore, multiple fault cores within the same structure can host both foreshocks and aftershocks during seismic sequences. All these observations suggest that fault zone structure exerts a primary control on the hydromechanical properties of faults.

To perform a detailed reconstruction of fault zone internal structure, we have integrated standard structural geology investigations with structural analyses obtained from a terrestrial laser-scanner survey. We have investigated the internal structure of the Tre Monti fault, a SSE dipping carbonate-hosted right-transtensional fault in the Central Apennines. The fault is exposed for a length of ~ 8 km and is ~ 1 km wide, with a throw of ~ 1500 m accommodated by at least three sub-parallel main slip surfaces.

Structural data have been gathered from exceptional exposures preserved within a quarry. In particular, the intensity and the orientation of joint sets within the damage zone were obtained both using a classical approach (i.e., scanline surveys on the quarry wall) and a semi-automatic extraction from the laser-scanner point cloud. Fracturing data were integrated with a detailed mapping of the secondary faults.

Fracture orientations extracted semi-automatically from the point cloud are consistent with data derived from scanlines, suggesting that once the appropriate calibration procedure is adopted, the laser scanner analysis is a valuable complementary tool in structural geology, capable of reproducing a huge amount of data in a short time.

The integrated analysis shows that secondary faults exhibit various orientations, from low angle antithetic normal faults to nearly-vertical oblique-slip faults with direction orthogonal to the main fault surface. They control local fracture density and geometry so that fractures are heterogeneously distributed within the quarry, with a density ranging between 10 and 50 m<sup>-1</sup> and do not show exponential increase approaching the main fault. In addition, a nearly-vertical joint-set with WNW-ESE to WSW-ENE direction is widespread. Such an orientation is consistent with the horizontal, approximately N-S trending,  $\sigma_3$  inferred from the right-lateral transtensional slip observed on the main fault surface.

Our preliminary data highlight a wide fault zone structure, formed by parallel fault cores that are surrounded by a complex network of fractures and minor faults with multiple orientations. Further studies on similar faults will be performed to develop a reference framework of fault-zone structure that can be useful for all the studies aimed at the characterization of the hydromechanical properties of carbonate-bearing faults.

# Radiometric ages of solid state deformation structures in the Northern Aadamello Avio granodiorite (Southern Alps, N Italy)

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Keywords: radiometric ages, pluton cooling, ductile shear zones.

Plutons intruded in evolving orogens are likely to undergo deformation during and after their cooling (e.g., Pennacchioni et al., 2006). Solid state deformation structures in the Avio pluton (Northern Adamello) include high temperature joints, ductile shear zones and pseudotachylyte bearing faults (Pennacchioni et al., 2006). Although the relative ages of deformation structures are clearly discernible from crosscutting field relationships, the absolute age and duration of each deformation phase cannot be constrained form structural analysis alone. We present here new <sup>40</sup>Ar-<sup>39</sup>Ar ages of the Avio granodiorite, ductile shear zones and pseudotachylytes, that help to clarify the temporal evolution of deformation style in a cooling pluton.

We analyzed biotite separates from the Avio granodiorite, bulk biotite-rich ultramylonite and pseudotchylytes sampled within the same magmatic body. Pseudotachylytes were sampled from two E-W trending faults: the Gole Larghe and Gole Strette faults. These faults dip steeply to the south and display a dextral transpressive kinematics. Ar-Ar measurements were preceded by detailed microstructural, geochemical and petrological analysis of the samples, including X-ray microtomography of the pseudotachylytes to select clast-poor samples for dating.

The granodiorite biotite was analyzed in the 71  $\mu$ m and the 1000  $\mu$ m granulometric fractions, which gave indistinguishable ages of 34.4 Ma, identical to the 34.7 ± 1.0 Ma Rb-Sr and K-Ar ages by Del Moro et al. (1983). The mylonite has an age of 32.9 ± 0.3 Ma, about 1.5 Ma younger than the granodiorite. All pseudotachylyte contain both plagioclase clasts from the granodiorite and late-stage alteration phases. The Ar-release steps reflecting the degassing of the pseudotachylyte matrix were identified by their homogeneous Cl/K and Ca/K signature, previously checked with EPMA analyses. Pseudotachylyte matrix gave ages of 30.4 ± 0.15 Ma and 30.3 ± 0.04 Ma, suggesting contemporaneity of the Gole Larghe and the Gole Strette faults. One of the samples included two generations of pseudotachylyte, aged 29.6±0.07 Ma and 25.2 ± 0.07 Ma.

Conclusions. (i) Ductile shear zones formed while the pluton was cooling during at least 1.5 Ma. The long cooling time requires an intrusion depth in agreement with literature estimates, ca. 10 km. (ii) Seismogenic faulting began about 4 Ma after pluton emplacement, in accordance with the results in Pennacchioni et al. (2006) and lasted for at least 4 Ma.

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### Deformation associated to shallow magma intrusions: hints from analogue models

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Keywords: analogue modeling, forced folding, supercritical.

Magma emplacing at shallow crustal levels may cause significant deformation in the overlying country rock (i.e., forced folding, fracturing and faulting), both at a local and/or regional scale. To get insights into these processes, we investigated in the laboratory the development of forced folds and associated fracture/ fault networks. An analogue magma, simulated by polyglycerols, was intruded into a sand pack representing the brittle crust. The scaled analogue models reproduced different 3D deformation structures depending on the model parameters (e.g., magma viscosity, injection rate, volumetric flux, and the rheology and thickness of the host and cover rocks). However, all models support the observation that the emplacement of shallow magmatic bodies may result in the growth of dome-shaped forced folds, and associated development of tensional and compressional deformation in the host-rock. Although the models involve simplifications, these results provide useful hints for geothermal research, as fractures and faults associated with magma emplacement can significantly influence the distribution and migration of superhot geothermal and/or ore deposit exploration. In this perspective, the results of analogue models may provide useful geometric constraints for field work, numerical modeling, and particularly seismic interpretation, allowing production and a better understanding of integrated conceptual models concerning the circulation of supercritical fluids.

The research leading to these results has received funding from the European Community's Seventh Framework Programme under grant agreement No. 608553 (Project IMAGE).

Montanari, D., Bonini, M., Corti, G., Agostini, A. & Del Ventisette, C. (2017): Forced folding above shallow magma intrusions: Insights on supercritical fluid flow from analogue modelling, Journal of Volcanology and Geothermal Research, 345, 67-80.

# Structural and stratigraphic constraints of the Cretaceous to Miocene deposits bracketing the forebulge unconformity in southern Apennines by means of extensional structures pattern and Sr-isotope stratigraphy

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Keywords: Forebulge, Sr-isotopes, fractures.

The main temporal constraints used so far in the Apennines to reconstruct the tectonic pulses are the ages of the foredeep deposits and the first unconformable wedge-top basin sediments. However, dating precisely these rocks has produced controversial results, mainly because they are generally poorly fossiliferous and dominated by reworked microfossils. A convenient alternative is dating with precision the first sediments overlying the forebulge unconformity, which are mainly represented by Miocene shallow-water carbonates. However, the biostratigraphy of shallow-water carbonates is plagued by low-resolution and poor chronostratigraphic calibration. By means of Strontium Isotope Stratigraphy (SIS) precise chronostratigraphic and numerical ages could be obtained for the base of these carbonates and the top of the substrate at different localities along the southern Apennine chain. Ages with precision in the 0.1-0.5 my range are obtained by SIS in Miocene and Cretaceous marine rocks and low-Mg calcitic bivalves.

In addition we performed a structural analysis of the bed-perpendicular fractures hosted both in the Cretaceous to Eocene pre-orogenic sequence and in the overlying Miocene syn-orogenic rocks. Overall, they are preferred oriented and characterized by the NW-SE, NE-SW, NNW-SSE/N-S and ENE-WSW/E-W trends. The abutting and cross-cutting relationships permit to distinguish forebulge and early foredeep fractures from pre-existent and later ones. In particular, the NNW-SSE/N-S and ENE-WSW/E-W -striking fractures could be related to the extensional deformation in the peripheral bulge area, which is associated with the bending of the downgoing lithosphere, characterized by systems parallel and orthogonal to the thrust front. Furthermore, some fractures are filled and sealed by Miocene calcarenites, predating these deposits and representing a clear example of deformation related to the forebulge flexuration.

The preliminary data obtained by means of SIS show an eastward youngering trend of the Miocene deposits overlying a pre-orogenic top sequence, which is older toward East in the southern Apennines. The dating results for the base of the Miocene shallow-water carbonates and the relative substrate are: upper Aquitanian for Cerchiara and Roccadaspide Fms (both sealing the Eocene Trentinara Fm; Alburno-Cervati-Pollino Mts); a range time not older than middle-upper Aquitanian for Recommone Calcarenites Fm (covering the Campanian-Santonian Calcari a Radiolitidi Fm; Sorrento Peninsula); Middle Burdigalian for the Cusano Fm (overlying the Aptian to upper Coniacian Calcari a Radiolitidi Fm; Matese-Camposauro Mts). This level of precision, never attained before in the Apennines, will permit to constrain the shortening rate by tracking the migration of the forebulge.

# Ultramafic rocks carbonation during paleo-seismic events: evidence from exhumed faults (Voltri Massif, Italy)

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Keywords: fluid-rock interaction, ultramafic rocks carbonation, fault zone.

Faults generally act as preferential pathways for fluids; the high fracture density within their damage zones can increase the host-rock permeability, enhancing the rock reactive surfaces and speeding-up fluid-rock interactions. Accordingly, fault zones, in the presence of an aqueous  $CO_2$ -rich fluid, could drive and enhance the natural carbonation of ultramafic wall rocks (peridotite and serpentinite); as a consequence, the drastic changes in lithology and mineralogy could also cause important variations in permeability and strength of the damage zone during deformation, through cycles of fault sealing.

Here we report of exhumed detachment zones occurring in peridotite and serpentinised peridotite (Voltri Massif, Ligurian Alps, Italy) that show evidences of paleoseismic activity combined with the cyclic precipitation of carbonates from CO<sub>2</sub>-rich hydrothermal fluids.

The damage zone of the studied faults contains different types of fault rocks, namely cataclasite, carbonated fault gouge, hydraulic breccias at the footwall and carbonated peridotite in the hangingwall. The fault cores are characterised by formation of a ca. 70 cm-thick cataclastic dolomite rich layer, containing dolomitic spherulites resembling the texture of cave pearls or ooolites with a serpentine core relic, but linked to the damage zone evolution. Cataclasites, containing damaged spherulites, are further cross-cut by carbonate coated slip zones and by chalcedony shear veins, with mirror-like surfaces, filamentous silica slickenlines, and granular injection veins, all of which provide evidence for paleoseismic activity.

We combined field data with microstructural (SEM-EDS, EBSD), mineralogical, geochemical (high-resolution elemental imaging by Laser Ablation-ICP Time of Flight-Mass Spectrometry,  $\delta^{13}$ C,  $\delta^{18}$ O analyses), and mass transfer calculations to characterise fully the mechanical behaviour of these faults, fluid-rock interactions during deformation and quantify the amount of CO<sub>2</sub> stored within the structure as hydrothermally precipitated carbonates.

# The role of inherited structures and slab flattening to the topographic growth of the Eastern Cordillera, Colombia

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Keywords: Inversion Tectonics, Thermochronology, Exhumation.

The growth of a mountain belt is commonly attributed to isostatic balance in response to crustal and lithospheric thickening. However, deeper mantle processes may also affect the topography of the Earth. Here, we discuss the role of these processes in the Eastern Cordillera (EC) of Colombia.

The EC is an active, double-vergent fold and thrust belt that formed during the Cenozoic by the inversion of a Mesozoic rift, and topography there has risen up to ~5000 m (Cocuy Sierra). The EC is located ~500 km away from the trench where the Nazca slab subducts below the South American plate. North of 5° N, the belt rises above a flat-slab subduction region. Volcanic arc migration suggests slab shallowing by ~ 10 Ma and flattening to the present configuration at ~6 Ma. The occurrence of a high  $v_p/v_s$  anomaly and clustered seismicity occurring below the belt at ~160 km depth delineate the slab geometry and have been related to dehydration of the slab, suggesting the presence of a hydrated mantle wedge.

We compiled available thermochronologic data and estimated the exhumation history of the belt over the last 20 Ma using an inversion method. The results indicate that exhumation rates increased during the Plio-Pleistocene at different wavelengths and amplitudes. Small wavelength and large amplitude signals could be related to shallow crustal deformation whereas long wavelength and moderate amplitude signals need to be addressed. These pulses of fast exhumation are concomitant with surface uplift occurring from  $\sim$ 7 Ma, as previously identified.

Combining structural and geophysical constraints for the crust and the mantle, we find that the observed high topography of the chain cannot be achieved solely through isostatic adjustment. Previous studies also suggested that positive residual topography matches the present-day elevation pattern of the belt. We propose that the recent uplift and long wavelength exhumation events were triggered by the transition from a regular to flat-slab subduction, along with the formation of a weak and buoyant wedge. We test the feasibility of our hypothesis with a series of numerical models and conclude that the recent topographic growth of the Eastern Cordillera is linked to slab-related mantle dynamics.

#### Controlling factors for the mode of slip in the shallowest portions of megathrusts

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#### Keywords: Megathrust Earthquakes.

Coseismic slip-to-the-trench, which occurred during  $M_w 9.0$  Tohoku-Oki 2011 earthquake, challenges the widely accepted paradigm of an aseismic nature of subduction megathrusts at shallow depths. In the new conceptual model, the frontal part of the subduction megathrust can support slip rates that range from plate convergence (mm/yr) to seismic (m/s) ones. The investigation of the conditions that favour slip-to-the-trench requires addressing a complex interplay of processes active from the trench down to 10-15 km depth along the subduction plate interface.

To investigate the shallow depth megathrust's co-seismic behaviour we have focussed on the geological framework for the development of the subduction megathrust. We combine friction experiments, energy balance calculations for rupture propagation, and numerical modelling for the elastic stress build up.

Our areas of investigation are the Middle America Trench offshore Costa Rica, and the Andaman-Sumatra Trench offshore Indonesia. In both places recent ocean drilling provided constraints on the geometry of the frontal part of the megathrust and samples of the lithologies involved in the shallow subduction. Although the incoming sediments are different, both areas are inferred to have experienced co-seismic slip to the shallowest part of the megathrust.

In this talk we review the results of high-velocity friction experiments conducted on incoming plate materials. It is well-known that the frictional evolution with slip and slip rate alone does not control the onset of seismic slip. To further explore whether the incoming plate sediments can store and release sufficient elastic energy to allow the fault to slip seismically, we used experimental data to estimate the energy available for seismic faulting and seismic wave radiation.

Lastly, we performed 2-Dimensional viscoelastic finite element numerical modelling to explore whether, given the stratigraphic and geometrical characteristics of the incoming plate sediments at the trench, (case 1) elastic strain can accumulate in the stronger material, or (case 2) the strain will be partly or completely released by creep in the adjacent weaker material. The results of the numerical models suggest that case 1 is possible when the incoming plate material bends and/or have geometrical complexity, such as faults. In this case stress distribution in the shallow megathrust becomes heterogeneous and is often accumulated where normal and/or reverse faults displace sediment layers.

#### Plastic to brittle deformations along the Meran-Mauls segment of the Periadriatic Fault, Italy

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Keywords: Periadriatic Fault, microstructures, paleostress.

The Periadriatic Fault (PF) is one of the most important tectonic element in the Alpine belt, separating the Europe-verging collisional wedge from the S-verging Southern Alps. This fault system developed in a dextral transpressional regime during the Cenozoic, following the Adria-Europe collision. The area between the Passeier and the Eisack rivers (Meran, NE Italy) is a key area for the understanding of the interactions among the PF, the Giudicarie Fault and the fault network here active in the Cenozoic (Viola et al., 2001). This region was extensively examined by us in the frame of the CARG project for the survey of the 1:50,000 Merano (Bargossi et al., 2010), San Leonardo and Vipiteno geological sheets of Italy in terms of geological setting, mesoscopic and microscopic structural analyses of fault rocks, and paleostress estimates.

In particular, the Meran-Mauls Fault segment of the PF, which connects the North Giudicarie Fault to the Pustertal segment of the PF, was deeply investigated and is the main subject of this contribution. Original structural information, integrated with the detailed analyses of representative cross sections, allow a better definition of the kinematic and structural evolution from the ductile to the brittle field. We integrated the analysis of this fault system with information on the kinematics of other important faults of the study area, including the Passeier, Faltleis, Val Nova and other minor faults. Our analyses suggest that the Meran-Mauls Fault and related structures show a progressive transition across the plastic-brittle transition with a marked reverse kinematics followed in time by a dextral transpression. Strike-slip to normal faults with different trends ranging from NW-SE to NE-SW follow in time. Paleostress reconstruction indicate a progressive switch of the main direction of compression from NW-SE to N-S, as suggested by us in the Central Alps (Agliardi et al., 2009).

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# **Session S10**

# The role of shear zones in the tectono-metamorphic evolution of the lithosphere: insights from microfabric to mountain belt structures

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# The competition between rates of deformation and solidification in syn-kinematic granitic intrusions: Resolving the pegmatite paradox

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Keywords: Melt-enhanced deformation, syn-kinematic granite, melt rheology.

Fully crystallized granites, rich in feldspar, serve to strengthen the continental crust, while their precursor melts are generally assumed to weaken the deforming crust and assist strain localization. Syn-tectonic granitic pegmatites within shear zones are commonly cited as evidence for magma-assisted rheological weakening - their precursor hydrous melts have especially low viscosities. Yet such pegmatites commonly reveal little internal deformation - implying they crystallized in the absence of tectonic shearing - but their shapes are indicative of them having deformed with a greater competence than their surroundings. This is the pegmatite paradox - their deformation as competent bodies implies that this happened after crystallization yet fully preserved igneous textures suggest deformation happened before crystallization. By describing and interpreting field relationships in a typical pegmatite/shear zone association (Torrisdale, NW Scotland), we suggest a mechanism by which syn-tectonic granitic melts may, in effect, act as competent bodies while still crystallizing. Crystallization can be pulsed as the concentrations of crystallization-inhibitors (fluxes) increase in residual fluids. Competence increase is enhanced by preferential crystallization on intrusion margins that serves to encapsulate residual melt inside stiff rinds. Modern estimates for the rates of feldspar crystallization (cms.a-1) from undercooled hydrous silicic magma to form pegmatites greatly outpace natural deformation rate estimates for shear zones. Preferential crystallization along rinds is evidenced by compositionally-zoned pegmatites together with interfacial buckling and boudinage. Zoned crystallization means that the bulk crystal concentration is not a guide to the bulk rheology of the melt-crystal composite. These relationships are typical of syn-kinematic granitic pegmatites, including those within the Nanga Parbat massif (NW Himalayas) - the type location for tectonic aneurysm models that invoke magma-enhanced deformation. The low initial viscosities of hydrous granitic melts promote long-range migration into higher crustal levels. In these undercooling conditions, rapid crystallization means fully-liquid melts may only be present fleetingly, during which time little significant strain can accumulate. Thus syn-kinematic hydrous granitic melts are irrelevant agents of weakening and their crystallized products strengthen shear zones.

# Dating the High Himalayan Discontinuity and the Main Cenral Thrust in the Marshyangdi valley (Central Nepal) by in-situ U-Th-Pb monazite petrochrnology

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Keywords: Collisional belt, Himalaya, shear zones, tectono-metamorphic discontinuities.

The mid-crust of the Himalaya is represented by the Greater Himalayan Sequence (GHS), one of the major tectonic units of the Himalayan belt exposed for nearly  $\sim 2500$  km. It has been considered as a coherent tectonic unit since long time, bounded by the South Tibetan Detachment to the top and the Main Central Thrust to the bottom. However, integrated studies by different techniques allow to recognise several high-temperature shear zones in the core of the GHS along the belt, with top-to-the S/SW sense of shear (High Himalayan Discontinuity: HHD, Montomoli et al., 2015). U-Th-Pb *in situ* monazite petrochronology provides ages older than the Main Central Thrust, along the same structural profile. Data on the pressure (P) and temperature (T) evolution testify that these shear zones affected the tectono-metamorphic history of the belt and different P-T conditions have been recorded in the hanging-wall and footwall of the HHD. This tectonic feature running for several hundreds kilometres is documented in several sections of Western and Central-Eastern Nepal dividing the GHS in two different portions. We present the results of a transect in the GHS of Marshyangdi valley (Manaslu massif, Pêcher, 1989). Close the transition between sillimanite-bearing gneiss and kyanite-bearing gneiss, few km north of Syangie village, we identified a high-temperature ductile shear zone with kinematic indicators pointing to a top-to-the S sense of shear.

U-Th-Pb *in situ* analysis on monazite, joined with chemical compositional maps, performed by LASS at Santa Barbara (California) on samples from the shear zone and its footwall provided ages ranging from ~ 8 to 43 Ma. The age of the HHD in the Marshyangdi valley is constrained between ~ 27 and 18 Ma, in very good agreement with the ages of the HHD detected along strike in the GHS (Montomoli et al., 2015; Carosi et al. 2018), before the later activation of the Main Central Thrust along the same section (Catlos et al., 2001; Gibson et al., 2016) constrained at ~ 16-13 Ma.

The occurrence of the HHD, detected by structural analysis and petrochronology, in the Marshyangdi valley allows us to fill a gap in the recognition of the HHD between Western and Central-Eastern Nepal.

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### 1:25.000 structural map of Lodè and Mamone in the northern of the Sardinian variscan basement

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Keywords: geological map, structural geology, Sardinian basement.

Sardinia consists of a Paleozoic Basement, intruded by Permo-Carboniferous granites and covered by Permian-Mesozoic sediments. The rotation of nearly  $90^{\circ}$  of the tectonic transport in Sardinia during collisional and post-collisional stages could be related to the paleoposition of the Corsica-Sardinia block close to southeast France (Maures-Tanneron Massif) (Corsini & Rolland, 2009). In Northern Sardinia two metamorphic complexes occur, recording similar deformation histories but different metamorphic evolution: the Low-Medium Grade Metamorphic Complex (L-MGMC) and the High Grade Metamorphic Complex (HGMC). The Posada Asinara Line (PAL) is a Carboniferous regional-scale transpressional shear zone Carosi & Palmeri, 2002) that crops out in northern Sardinia, separating the two latter complexes, playing an important role in the exhumation of the metamorphic complexes (Carosi & Palmeri, 2002). The survey's area between Lodè, Sant'Anna and Mamone (NE Sardinia), in the southern part of the PAL, allowed to refine previous geological maps (Carosi et al., 2005). A structural-geologic survey has been carried out in an area about 200 km<sup>2</sup> and a new geological map (1:25000 scale) has been realized. The principal structural asset is characterized by F2 north-vergent folds, associated with the progressive development of a mylonitic principal foliation. The structural analysis highlighted four deformation phases. The D<sub>1</sub> phase has been observed only inside the quartz layers and in the para-gneiss levels, that are folded but not completely transposed during the D, deformation phase. The prominent deformation phase, D<sub>2</sub>, is associated with isoclinal and N-vergent F<sub>2</sub> folds. The S<sub>2</sub>axial plane foliation strikes N70-110° with variable dip but generally steeply dipping. A, fold axes trend nearly E-W with variable shallow plunge. An elongation lineation trending nearly E-W and plunging between 5° and 20° occur on the S<sub>2</sub> foliation. D, rotational component increases moving to the North and kinematic indicators (S-C-C' fabric, mica fish, rotated porphyroclasts) indicate a dextral sense of shear (top-to-the NNW). The D<sub>3</sub> phase is often associated to a crenulation cleavage (F<sub>3</sub>), and mainly chevron folds. D<sub>2</sub> and D<sub>3</sub> fold axes phases are generally coaxial, but with perpendicular axial plane. The  $D_4$  phase is associated with open folds  $F_4$  with sub-horizontal axis and axial planes, almost oriented SSE-NNW, but with a considerably axial dispersion, without the formation of an axial plane foliation. These folds cause the change of dip from S to N of the S<sub>2</sub>. Thanks to this detailed survey, associated to a microstructural study, it has been observed how the isograds, marked by the blastesis of the principal Barrovian minerals (biotite-garnet-staurolite-kyanite) in field are folded and stretched during D, deformation (Mamone and Lodè synforms). Isograds are telescoped approaching the high-strain zone due to combined effect of simple and pure shear acting during D<sub>2</sub> (Iacopini et al., 2008).

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### P-T-t-D paths of the Cuonadong detachment, SE Tibet

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Keywords: Cuonadong, gneiss domes, Petrochronology.

The Cuonadong gneiss dome (SE Tibet), located in the south-eastern part of the north Himalaya close to the South Tibetan Detachment System (STDS) to the south, is a gneiss dome of the North Himalayan Gneiss Domes (NHGD), identified recently (Fu et al., 2017). It divided into three main tectonic units separated by an upper brittle detachment and a lower ductile one. The upper tectonic unit, above the upper brittle detachment, is made by unmetamorphosed to low-grade metamorphic Jurassic-Lower Cretaceous slate, metasandstone and phyllite. The middle tectonic unit, sandwiched between the upper and lower detachments, mainly consists of highly deformed micaschist, marble, granite and pegmatite. The middle unit mainly consists of chloritoid-garnet micaschist and minor two-mica schist. The lower tectonic unit consists of mylonitic gneiss, leucogranite plutons, dikes and sills. Meso- and microstructural analysis revealed that the Cuonadong dome records four main phases of deformation: D1, related to top-to-the S shearing, D2 related to N-S extension, D3, linked to E-W extension, and D4 related to the later collapse of the dome.

Pressure (P) - Temperature (T) conditions and P-T-deformation paths for selected sample were derived with the aid of pseudosections in the MnNKCFMASHT system. The selected sillimanite-staurolite-garnet micaschist, from the lower detachment, underwent D2 deformation and contains garnet showing prograde compositional zoning and yielding P - T estimates of 6.0-7.0 kbar and 520-670°C.

The Laser-Ablation-Split-Stream (LASS) *in situ* U-(Th)-Pb monazite geochronology, of this selected sillimanite-staurolite-garnet micaschist constrains the prograde Barrovian metamorphism at ~26 Ma. We constrain the activity of the Cuonadong lower ductile detachment, during retrogade metamorphism in the sillimanite stability field to ~ 21 Ma.

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### Structural setting of the Yalaxiangbo dome, SE Tibet (China)

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Keywords: HImalaya, North Himalayan Gneiss Domes, shear zones.

The Yalaxiangbo gneiss dome (SE Tibet) in eastern Himalaya is one of the major metamorphic culminations in the Tethyan Himalayan Sequence, referred to as North Himalayan Gneiss Domes (NHGD). It comprises three main tectonic units separated by an upper ductile/brittle and a lower ductile detachment. The upper tectonic unit, above the upper ductile/brittle detachment, includes unmetamorphosed to low-grade metamorphic Triassic-Lower Cretaceous slate and metapsammite of the Tethyan Himalayan Sequence. The middle tectonic unit, sandwiched between the upper and lower detachments, consists of mylonitic granite, staurolite-garnettwo mica schist and biotite-plagioclase gneiss affected by the ductile top-to-the north extensional shear of the lower detachment. The lower tectonic unit consists of mylonitic gneiss, leucogranite plutons, dikes and sills.

By integrating macro-/micro-structural analyses, petrographic and Laser Ablation Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) *in situ* U-(Th)-Pb monazite geochronological data from selected samples affected by ductile shear, we constrain the activity of the lower detachment at *c*. 18 and the shearing along the upper detachment later than *c*. 15 Ma (Chen et al., 2018). The detachment system is made up by two different shear zones activated in different times and at different structural levels and our data are in agreemt with a migration of the deformation from the lower portions to the upper ones (Kellet & Grujic 2012, Cottle et al., 2015, Iaccarino et al., 2017, Montemagni et al., 2018). The kinematic, geochronology and petrologic features of the Yalaxiangbo detachments are similar to the South Tibetan Detachment system, which crops out in southern Tibet.

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#### Post-Variscan events recorded near the Pogallo line (Lago d'Orta)

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Keywords: Southern Alps, rifting, partial melting.

The Pogallo line is a ductile shear zone affecting the basement of the westernmost part of the Southern Alps and consisting of mylonites developed under amphibolite to greenschist facies conditions. It is considered as a midcrustal extensional listric fault that accommodated extension during the Alpine Tethys Jurassic rifting (Handy et al., 1999). More recently, it has been interpreted as part of the "necking fault system" of the Adriatic rifted margin (Decarlis et al., 2017). In order to check the presence of post-Variscan (pre-Alpine) events near the Pogallo line, a field and petrographic study of the Strona-Ceneri Border Zone (SCBZ) has been carried out in the area near Omegna and Pella (western side of the Orta Lake).

The SCBZ is located between the meta-arenites of the Strona-Ceneri Zone and the meta-pelites of the Scisti dei Laghi. It consists of banded amphibolites and paragneisses with lenses of ultramafic rocks, metagabbros and retrogressed eclogites (Giobbi Origoni et al., 1997).

In the studied area, the SCBZ consists of medium-grained banded amphibolite with lenses of coarsegrained amphibolite, serpentinite - surrounded by Tr-Chl-Tlc-metasomatites - aplitic orthogneiss, and a layer of "feldspathized amphibolites". A paragneiss layer usually occurs at the contact between the SCBZ and the Ordovician orthogneiss.

The Variscan foliation is well preserved in both coarse- and medium-grained amphibolites and in para- and orthogneisses but, noteworthy, not in serpentinites and related metasomatites. Evidences for post-Variscan events are: (i) an high-temperature stage characterized by partial melting of coarse-grained amphibolites, melt impregnations in medium-grained amphibolites, high temperature mineral assemblage (Sil, Crd, Kfs) in both para- and orthogneisses, intrusion of undeformed aplitic dykes in paragneiss; (ii) serpentinization and related metasomatism possibly connected with the fluid/melt circulation; iii) a subsequent mylonitic event at amphibolite-facies conditions recorded only in the medium-grained amphibolite.

Thus, our data indicate a post-Variscan heating event followed by an amphibolite-facies mylonitic stage localized near the Pogallo line. The in-progress study on such events may provide new insights on the development of the Pogallo shear zone and may help to enhance the comprehension on the necking-related processes.

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### Alpine shear zone reworking Variscan rocks in the Sila Piccola Massif (Northern Calabria)

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Keywords: Alpine reworking, Sila Massif, poly-orogenic evolution.

Petrological and microstructural investigations focused on a portion of the lower-intermediate continental crust of the Calabrian crystalline basement have been carried out near the village of Castagna (northern Calabria). In particular, a mylonitic horizon affecting granulite facies rocks of the Sila Unit has been studied and an Alpine metamorphic shearing imprint superposed on earlier high temperature Variscan relics has been recognised. Such earlier preserved assemblages, occurring as low strain domains of garnet-sillimanite paragneiss within the pervasive mylonitic foliation, consist of intermediate to low Ti-biotite and oligoclase-andesine plagioclase. The compositional garnet profile indicates a likely re-homogenisation of cores suggesting a long time residence at high T conditions in the lower crust. A subsequent Alpine mylonitic overprint generates retrograde metamorphism at upper amphibolite facies conditions possibly representing a "detachment zone", responsible for the exhumation of the deepest parts of the continental crust, reworked during the building of the Alpine Orogen.

# Microtomography investigation of ultramylonites from crustal scale shear zones and implications on the rheology of the continental lithosphere

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Keywords: X-ray computed tomography, mylonite, 3D petrofabric.

Recognition of different constituting phases and their volumetric distribution in different portions of the same deformed rock are crucial constraints to develop models for rock rheology. A 3D microstructural study of ultramylonites sheared under opposite deformational regimes (compressional vs extensional) developed within different crustal scale shear zones has been performed. Two sites have been selected as natural laboratories for investigating the mylonitic evolution of rocks during the shearing event: Montalto Shear Zone (MSZ, Italy; Fazio et al., 2015; 2018a) and Kavala Shear Zone (KSZ, Greece; Punturo et al., 2014; Fazio et al., 2018b). These rocks are characterized by extremely fine grain size of matrix as well as by small porphyroclasts. Matrix-constituting minerals, such as quartz, feldspars and micas form an interconnected network testifying high strain conditions, which affects the rheological behavior of the shear zone at depth. Therefore, our aims are to investigate the mylonitic fabric at the micro-scale by quantifying the appearance of new mineral phases at increasing matrix/ porphyroclasts ratio as well as the 3D development of matrix network and the variations in Shape Preferred Orientations (SPO) of constituent minerals, with particular regards to dynamically recrystallized new grains, few microns sized. These features can be well investigated by 3D analysis of their morphology and distribution by X-ray computed tomography (CT) technique. On investigated samples, the microtomography analyses provided detailed 3D information about clasts (volumetric distribution, grain sizes, phase interconnectivity), permitting to fully investigate the 3D distribution and arrangement of minerals, with particular regards to grains (few microns sized) of the matrix. Further investigations and 3D data rendering elaborations will allow us to formulate realistic models about grainsize reduction processes induced by deformation within such rocks.

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### Shear-related production of fake granitoids: there are trondhjemites and trondhjemites in the southern Calabria-Peloritani Orogen

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Keywords: Variscan shear zones, fluid-rock interaction, NE Sicily.

Late Variscan trondhjemites and granites make up small plutonic complexes intruded in migmatitic paragneisses in the northeastern Peloritani Mountains (southern Italy). In particular, two different varieties of trondhjemites occur: s.s., with typical CaO contents (>1.5 wt%), and low-Ca, with lower CaO contents comparable with those of the granites. Furthermore, trondhjemite sub-varieties with anomalous Na<sub>2</sub>O and K<sub>0</sub>O contents also occur. The s.s. trondhjemites and the granites have petrographic and geochemical features consistent with generation by water-fluxed and dehydration melting of metapelitic rocks, respectively. Low-Ca trondhjemites show significant similarities with the granites, but are characterized by massive subsolidus crystallization of turbid plagioclase at expense of magmatic K-feldspar. Secondary plagioclase is present in different amounts in all rock types, but it appears as an important rock-forming component only in the low-Ca trondhjemites, indicating these rocks as the product of infiltration metasomatism of the associated granites. All the granitoids were affected at varying extents by shear-related deformation that, in the most strained samples, resulted in significant tectonic grain size reduction, therefore producing an increase of the rock permeability as well as a parallel increase of the surface-controlled rock reactivity. Shear-zone activity played a significant role in driving the metasomatic modifications, as documented by nearly ubiquitous examples of secondary plagioclase growing along micro-shear zones filled with new grains of quartz and feldspars. Furthermore, occurrence in many granitoid samples of chessboard patterns in quartz indicates high-temperature deformation of more than 650 °C. Such high shearing temperatures suggest shear-zone activity at the same time or soon after the emplacement of the late Paleozoic plutons. Late Variscan shearing deformation starting at submagmatic conditions, during the cooling of the c. 310-300 Ma Aspromonte-Peloritani granitoid bodies, is consistent with the activity of the crustal-scale shear zone that controlled the emplacement of the 13-km thick Serre Batholith (central Calabria), between c. 300 and 290 Ma. This context provides viable conditions for pervasive fluid migration across the sheared crust, as well as a possible source for the metasomatizing fluids, that could have been released during crystallization of the huge volumes of granitic magmas of the Serre Batholith. Since metasomatic replacement of feldspar is largely pseudomorphic, its original magmatic habit is often preserved and, at the same time, most derived bulk rock geochemical features can be interpreted as reflecting igneous processes. This leads to the final consideration that shear zones can drive large-scale metamorphic reactions able to produce deceptive metamorphic rocks that pretend to be magmatic.

### Inverted metamorphic sequence along the Alaknanda-Dhauli Ganga valleys, Garhwal Himalaya (NW India)

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Keywords: Inverted metamorphic sequence, Himalaya, shear zone.

One of the most common and peculiar features of the Himalaya, resulting from the collision between India and Eurasia plates at *c*. 55 Ma, is the development of an inverted metamorphic sequence (IMS) along the Main Central Thrust zone (MCTz), the tectonic boundary between two main litho-tectonic units, i.e. the Greater Himalayan Sequence (GHS) and the Lesser Himalayan Sequence (LHS). This regional boundary, the MCTz, corresponds to a km-wide contractional ductile to brittle-ductile shear zone where an increase of pressure-temperature conditions is present moving structurally upwards. The Alaknanda-Dhauli Ganga valleys (Garhwal Himalaya, NW India) are Himalayan regions of where a large dataset, consisting of geochemical, isotopic and geochronological data structural, microstructural and petrofabric observations and petrologic estimates (Hunter et al., 2018a,b; Jain et al., 2014 with references) is present for the MCTz. Particularly, in this area the MCTz was mapped as a delimitated by two discrete thrusts, the Vaikrita Thrust at the top and the Munsiari Thrust at the bottom (e.g., Valdiya, 1980). Despite this large dataset, there are still open questions regarding, for instance, the MCTz structural evolution and the possible reasons for the development of an IMS.

In this contribution a detailed meso- & micro-structural and petrological reappraisal along the MCTz transect is presented, focusing also on the distribution of index-minerals and the relationship between blastesis and deformation.

The metamorphic evolution of selected key-samples along the MCTz has been reconstructed after detailed electron microprobe work using multi-equilibrium geothermobarometry, P-T grids and equilibrium assemblage diagrams. U-(Th)-Pb *in situ* monazite geochronology allowed us to put an absolute temporal constraint both on the prograde metamorphic history and on the exhumation-related metamorphic overprint of the upper part of the MCTz. Our results, in agreement with previous studies, show how along the MCTz a clear inverted metamorphic gradient (from c. 500 up to c. 700°C) is well constrained and, particularly, it is also discernable by the distribution of Al-rich minerals (e.g., chloritoid, staurolite, kyanite) in sheared impure quartzite, often "ignored" for P-T estimates. On the contrary, obtained "peak" temperatures along the MCTz are only partially in agreement with the published (lower) T suggested by microstructural-based thermometry. Nevertheless, since available geochronology suggests that "peak" temperatures along the profile were reached at different times an intense contribution of shear heating for the development of IMS in this part Himalaya is not likely (Duprat-Oulid and Yamato, 2017). These new P-T-D-t data, joined with the data available in the geological literature, shed new light on the tectono-metamorphic evolution of the Himalayan metamorphic core in this portion of the belt.

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#### Contemporaneity of the STDS and MCT in Garwhal Himalaya (NW India): myth or reality?

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Keywords: Himalayan belt, Main Central Thrust zone, South Tibetan Detachment System.

In the Himalayan belt the contemporaneity of the South Tibetan Detachment System (STDS) and the Main Central Thrust zone (MCTz) has long been believed (Beaumont et al. 2001) to be the main mechanism for the exhumation of the metamorphic core of the belt, the Greater Himalayan Sequence (GHS).

As constraining the timing of activity of the MCTz and the STDS is a key task to understand Himalayan tectonics, many studies have focused on these two opposite-kinematics shear zones. However, their age of motion is still debated because each study focused on different geological features and the geochronological data are controlled by deformation and prograde and retrograde reactions. We report a multidisciplinary approach based on detailed microstructural, chemical and geochronological investigations in order to constrain the activity time of both the STDS and the MCTz in the Alaknanda - Dhauli Ganga valleys (Garhwal, NW India) along the same transect using the same analytical and interpretive approach. The MCT *sensu stricto* in the study area is named Vaikrita Thrust.

Microstructural observations of the STDS reveal different deformation features from the uppermost sample to the lowermost one paired with decrease in muscovite <sup>40</sup>Ar/<sup>39</sup>Ar ages, which is deformed in the uppermost sample and is undeformed in the lowermost one. Muscovite ages vary from c. 16 Ma down to c. 14 Ma structurally downward (Montemagni et al. 2018a).

Vaikrita Thrust rocks show three microstructurally distinct mica generations in different structural domains: a relict foliation only locally preserved, a main mylonitic foliation, and a late generation of coronitic micas around garnet. Combining microstructural, chemical and <sup>40</sup>Ar/<sup>39</sup>Ar data with Ca-Cl-K correlation diagrams we infer that the growth of mica along the main mylonitic foliation occurs at c. 9 Ma, whereas formation of undeformed coronitic muscovite yields c. 6 Ma (Montemagni et al. 2018b). Our results demonstrate a true non-contemporaneity of STDS and MCT in the Garhwal Himalaya: the shearing along the MCT continued at least 7 Ma later after the cessation of shearing on the STDS. Any model of exhumation of the GHS should account for this lack of contemporaneity.

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# Deformation and kinematics in the South Tibetan Detachment System (Himalaya): a telescoped regional "contact" metamorphism?

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Keywords: Himalaya, non-coaxial flow, South Tibetan Detachment System.

The South Tibetan Detachment System (STDS) is a system of regional ductile-to-brittle top-to-the E and NE normal shear zone and faults developed for more than 2000 km along the Himalaya strike. The STDS gets in contact the very-low- to low-grade metamorphic rocks of the Tethyan Himalayan Sequence (THS), in the hanging-wall, from the medium to high-grade metamorphic rocks of the Greater Himalayan Sequence (GHS), in the footwall. We investigate, four different sections of the STDS cropping out from West to East in Lower Dolpo (western Nepal), Kali Gandaki and Marsyangdy valleys (central Nepal) and Dinggye area (south Tibet)

The ductile shear zone is very well developed in all the study sections and it affects both tectonic units, i.e. THS and GHS. Due to the carbonate-rich nature of THS and GHS rocks along the study transects, identifying and mapping the STDS is not a simple task.

Along all the structural sections, we densely sampled impure marble and calcilicate from both units deformed by the STDS related ductile-shearing.

Ductile deformation is heterogeneous, leading to the development of calcmylonites associated to a mylonitic foliation striking parallel to the STDS and dipping at low-angle to the N and NE. All kinematic indicators confirm a top-to-the N and NE sense of shear.

Finite strain analyses have been performed in marbles on sections parallel to XZ plane of finite strain ellipsoid and point out to a finite strain increase moving from top to bottom. Microstructural and petrofabric analysis of calcite and quartz was carried out and reveal both SPO and LPO in almost all samples, supporting intracrystalline creep and dynamic recrystallisation as main deformation mechanisms.

Vorticity of flow (Wk), estimated by different vorticity gauges, highlights a non-coaxial deformation regime, with a main pure shear component, acting during the STDS activity both in high- and medium-temperature and low-temperatures mylonites. In addition a condensed metamorphic field gradient has been clearly detected though deformation mechanism and microstructures. The shortening perpendicular to the shear zone is also responsible for the telescoping of the metamorphic isograds at the base of the THS due both to shear heating and heating from the lower and hotter GHS.

# Structural setting, kinematics and metamorphism in a km-scale shear zone i n the Inner Nappes of Sardinia (Italy)

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Keywords: Variscan belt, palaeopiezometry, shear zone.

In continental collisional orogenic belts, the hinterland-foreland transition plays a crucial role in the deformation styles and in the exhumation modes of the middle crustal rocks. The Barbagia Thrust (BT), a regional scale shear zone in the Variscan belt of central Sardinia, represents this transition. The BT, separating nappes with different deformation styles, is still poorly characterized. We present new data of the BT and of the nearby tectonic units, using a multidisciplinary approach. We characterized in detail both meso- and microstructural features, as well as, the metamorphic conditions with the aid of illite and chlorite "crystallinity" of rocks from the footwall, hanging wall and high-strain zone of the BT. Moreover, combining different palaeopiezometer-wet quartzite flow law pairs we characterized the rheological parameters (i.e., flow stress and strain rate) present during the BT activity. Three main deformation phases were recognized. After a D1 contractional deformation, a D2 related to the BT movement was associated to the development of a nearly 100 m thick high-strain zone with the development of a mylonitic foliation, Sm, at middle crustal conditions, near the "brittle-ductile" transition. Metamorphic constrains obtained from the footwall, the hanging wall and the high-strain zone supported an epizonal metamorphism with no unambiguous trend related to the strain intensity. Integrating our new metamorphic, deformation and rheological data, with previous ones in the geological literature helps to better unravel the long-lasting history of the nappe emplacement at hinterlandforeland transition in the Sardinian Variscan Belt.

# Non-coaxial deformation of the Main Central Thrust zone: kinematics and temperature regimes in the Annapurna Range, Lower Dolpo Region (Western Nepal)

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Keywords: Himalaya, shear zone, petrofabric.

The Himalayan belt is a natural laboratory for studying exhumation processes because of the lateral exposure for nearly 2500 km of main structures and units, affected by a still active N-S convergence. An important feature of the chain is the occurrence of a mid-crustal metamorphic core, the Greater Himalayan Sequence (GHS), bounded by a top-to-the-S shear zone at the base, the Main Central Thrust zone (MCTz), and by a "contemporaneous" low-angle top-down-to-the-N/NE extensional complex of shear zones at the top, the South Tibetan Detachment System (STDS). These two opposite shear zones are related to the extrusion of the GHS, that is tectonically sandwiched between the low- to medium-metamorphic grade Lesser Himalayan Sequence (LHS) at the base and on the low- to non-metamorphic Tethyan Himalayan Sequence (THS) at its top. Moreover, the GHS is deformed by a system of ductile contractional top-to-the-S high-temperature shear zones (High Himalayan Discontinuity, HHD), which makes the GHS of additional interest in studying exhumation processes for deep-seated metamorphic cores (Montomoli et al., 2013).

In this work, we focused on the hangingwall rocks of MCTz along a N-S transect near Dunai, in the Lower Dolpo Region (Western-Central Nepal), where several kinematic indicators confirm a top-to-the S sense of shear (Carosi et al., 2010). From south to north, kyanite + garnet paragneiss are followed by sillimanite + garnet quartz-rich mylonites, suggesting a northward increase of deformation temperature as also supported by chessboard microstructures in quartz and myrmekites in feldspars in structurally higher located samples. Petrofabric analyses of quartz, developed by an X-ray Texture Goniometer (X'Pert Pro MRD\_DY2139 by PANalytical), indicate a strong crystallographic preferred orientation (CPO) coherent with a non-coaxial plan strain regime, where the asymmetric distributions of c-axes point to a top-to-the S sense of shear connected to the MCT kinematic. Furthermore, prism and prism are the main active slip systems in upward samples, whereas rhomb and basal slip systems dominate at the base of the GHS, inferring that dislocation slip acted as the main deformation mechanism during deformation flow with increasing temperature from the bottom to the core of the GHS. The petrofabric emphasises, together with mineral assemblage and microstructures, the inverse metamorphic field gradient at the bottom of the GHS in the Lower Dolpo region.

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# Brittle reactivation of mylonitic shear zones: constraining the Cenozoic tectonic evolution at the Transantactic Mountain Front, Victoria Land, Antarctica

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Keywords: Transantactic Mountains (TAM), West Antarctic Rift System (WARS), Cenozoic.

The Transantactic Mountains (TAM) form the western boundary of the West Antarctic Rift System (WARS), one of the largest continental rift domains on Earth, starting in the Mesozoic and still active today. The TAM are commonly regarded as the most prominent topographic expression of a rift-related, shoulder uplift on Earth.

It is largely recognized that Cenozoic TAM evolution occurred in a context of transtensional dextral tectonic regime. Brittle deformation is generally diffuse and not focused along master faults that probably are hidden by glaciers. Throughout the entire TAM, the mapped Cenozoic faults are always oblique with respect to the TAM margin. In this context still debated is the role of the structural inheritance, the synchronicity between faulting and uplift, and the processes responsible for shear strain localization in the brittle crust.

During the last Italian Antarctic Campaign (November 2017), a number of 593 structural data related to brittle fault planes and associated slickenlines have been collected in 32 geo-referenced sites in the region to the south of the David Glacier, where various granitoid bodies of the Granite Harbour Intrusives crop out. Fault arrangement shows a predominance of dextral, trastensional faults kinematics along sub-vertical, NW-SE to N-S striking fault strands, coherently with previous field studies along the TAM front. Most of the brittle faults localise and re-work a pre-existing steeply-dipping mylonitic fabrics, typically producing cm- to m-thick cataclastic bands. The mylonitic fabrics vary from proto- to ultra-mylonite. The shear foliation is characterised by the syn-kinematic growth of biotite in association with quartz ribbons in the high strain domains. Quartz grains diplay patchy undulose extinction, subgrains and subgrain rotation recrystallization; feldspar is porphyroclastic. Collectively, the textural evidence indicates syn-greenschist faciesmetamorphic conditions during the mylonitic shearing (deformation temperature <400 °C). The structural evidence of transition from ductile-to-brittle dominated shearing along the TAM front will provide an exceptional archive of information for the understanding the spatio-temporal scales and physical-chemical processes involved in the Cenozoic tectonic reactivation of the Gondwanian continental crust of East Antarctica.

# Rheology and kinematics of the early-Alpine strike slip tectonics in the southern Calabrian terrane: the case of the Palmi shear zone (southern Italy)

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Keywords: Mylonitic skarns, Image analysis, Quantitative microstructural analysis.

The Paleocene early-Alpine drifting of the Kabilo-Calabride crystalline basement microplate was controlled by deep rooted strike-slip tectonics, developing several crustal-scale shear zones which accommodate part of the African verging transport of these internal sectors of the Paleo-Alpine realm. Such tabular high strain zones played a key role in the mountain building processes of the Alpine belt, and determined kilometric offsets of crustal blocks at the lithosphere scale. Some of these rooted mylonitic horizons were successively exhumed and involved in Oligocene-Miocene late-Alpine brittle tectonics. One of the relics of this early-Alpine strikeslip tectonics occurs between the Serre and the Aspromonte massifs (Cirrincione et al., 2015) along the roughly oriented E-W Palmi-Antonimina tectonic alignment (Prosser et al., 2003; Ortolano et al., 2013; Festa et al., 2016). This consists of 400 m wide sub-vertically foliated Variscan mylonitic rocks that mainly comprise skarns with subordinate migmatitic paragneisses and tonalites. The mylonitic horizon is extended inland for about 1500 m from the Tyrrhenian coast near Palmi village, and divides biotite migmatitic paragneisses to the north from continuous exposures of tonalites to the south.

New mesostructural data have been mapped on a highly detailed (1:5000 scale) topographic base. This new structural map allows us to highlight the dominant kinematics of the plastic flow. The shear zone shows a complex geometry characterized by decameter-sale sheath folds (Fazio et al., 2017), and low strain domains comprising cm- to m-sized tonalite blocks, which often show opposite senses of shear. In order to unravel the main shear sense of the strike-slip plastic flow, the axial-planar intersection method (AIM) was applied to minor S- and Z-type folds (Alsop & Holdsworth, 2007). In addition, new quantitative microstructural investigations have been carried out through the acquisition of  $\mu$ -XRF maps and high-resolution scans of entire thin sections, to obtain detailed mineral modal and mineral size distribution maps. These data have been integrated with new grain boundary maps of the sin-mylonitic quartz-rich domains allowing estimates of both paleostress and the dominant shear-type (pure vs simple shear).

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### Strike-slip fault shear vs. mega-block drift in Yunnan (China): paleomagnetic and structural investigation

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Keywords: Paleomagnetism, Gaoligong shear zone, Strike-slip fault.

A wealth of paleomagnetic data from Yunnan (China) showed in the past a predominant post-Cretaceous clockwise (CW) rotation pattern, mostly explained invoking huge (hundreds of km wide) blocks, laterally escaping (and/or rotating) due to India-Asia collision, separated by major strike-slip shear zones. We report on the paleomagnetism of the outcrops close to the Gaoligong dextral shear zone. Fifty paleomagnetic sites (503 samples) were sampled at variable distances (up to ~25 km) from mylonites exposed along the Gaoligong fault. Jurassic-Cretaceous red bed sites yield systematic CW rotations with respect to Eurasia that peak at maximum (176°) close to the fault, and progressively decrease moving eastward, up to be virtually annulled ~20 km E of mylonite contact. West of the fault, Pliocene-Holocene sites from the Tengchong volcanic field do not rotate.

Thus, our data show that Gaoligong shear zone activity yielded significant CW rotations that were likely coeval to the main Eocene-Miocene episodes of dextral fault shear. The Gaoligong zone rotation pattern conforms to a quasi-continuous crust kinematic model, and shows blocks of  $\leq 1$  km size close to the fault, that enlarge moving eastward. Rotation values and width of the rotated-deformed zone translate to a 230-290 km Gaoligong shear zone dextral offset. Our work shows that fault shear plays a significant role for Indochina CW rotation occurrence.

The data do not support a rigid block rotation, but suggest the blocks to be made of small (few km of size) sub-blocks rotating, separated by non-rotating domains of similar size. Our data, along with previous paleomagnetic and tectonic evidence, show that crust deformation of the Yunnan is extremely complex and still to be completely elucidated. Also other blocks underwent strong internal deformation and were likely fragmented in smaller independent sub-blocks, whose kinematics and tectonics are still a matter of speculation.

# Kinematic of the flow and finite strain analysis in the Cavalaire Fault (Maures Massif, SE France) and in the Posada-Asinara shear zone (Sardinia basement, Baronie)

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Keywords: mylonites, shear zones, Variscan basement.

The Maures-Tanneron Massif (MTM) is the southernmost branch of the Variscan Belt in France (Corsini & Rolland, 2009). It was separated from the Corsica-Sardinia block because of the anticlockwise rotation related to the opening of Mediterranean back-arc basin during Miocene. Both in the Sardinian variscan basement and in the MTM two different metamorphic complexes are recognized: a low-medium grade metamorphic complex and a high-grade one. In both context the two complexes are divided by a regional-scale ductile shear zone. The correlation between these two shear zones is still debated and, at the moment, it is based mainly on petrographic similarities. Microstructural study, kinematic of the flow and finite strain analysis were performed on mylonites both from the Cavalaire Fault cross-cutting the Maures Massif and on the Posada-Asinara Line in the Sardinian Variscan basement (Carosi & Palmeri, 2002; Carosi et al., 2012). Kinematic vorticity analysis was performed with the C' shear bands method (Kurt & Northrup, 2008) and the stable porphyroclasts method (RGN) (Passchier, 1987; Wallis et al., 1993). The angle  $\theta$ , between the maximum Instantaneous Stretching Axis (ISAmax) in the horizontal plane and the shear zone boundary, was also calculated. The finite strain analysis was performed on some oriented samples collected within the mylonitic belt from both Shear Zones, on the XZ and YZ planes of the finite strain ellipsoid. We used garnets and K-feldspar porphyroclasts strain markers. The data allowed us to reconstruct the finite strain ellipsoid. Combining the Wk value and finite strain parameters (Law et alii., 2004), we calculated the percentage of shortening and stretching perpendicular and parallel to the two mylonitic belts. The structural asset of the Cavalaire Fault and its metamorphic evolution are very similar to the structural setting and the metamorphic evolution of the Posada-Asinara shear zone in the Sardinian Variscan basement (Carosi et al., 2012). Both shear zones are characterized by a transpressional deformation with the same kinematic developed during anfibolite-facies metamorphism. The new data about finite strain and kinematic of flow of the Cavalaire Fault and Posada-Asinara Shear Zone strengthen the correlation between these two Variscan basements.

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## The ductile deformation in the Messinian terrigenous deposits on top of the Inner Apulian Platform (Monte Alpi, Basilicata)

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Keywords: Mylonites, Ductile deformation, Southern Appennines.

Mylonites are generally found in basement complexes, where strain localization within shear zones takes place at amphibolite to greenschist facieses. More rarely, calcite mylonites develop at low-grade to anchizonal conditions in the external portions of the orogenic belts. In this work, we document a shear zone characterized by mylonites that formed in the upper diagenetic zone from a sedimentary protolith of Messinian age. Mylonites are documented at the top of the Apulian carbonates of the Monte Alpi Unit, southern Apennines, at the contact with overlying allochtonous units. In particular, these structural elements are present within sandstones and conglomerates originally deposited in a foreland basin system. These sedimentary rock were buried down to ca. 5 km, during the Early Pliocene emplacement of the fold-and-thrust belt over the Apulian carbonates, and then exhumed during Late Pliocene low-angle normal faulting and then Middle-Pleistocene-Holocene high-angle faulting.

The present study focuses on both meso- and micro-scale structural analyses of the aforementioned mylonites, which represent the major regional detachment horizon of the southern Apennines fold-and-thrust belt. The protolith is mostly made up of laminated sandstones, which include isolated conglomerate bodies, is up to ca. 200 m-thick, and made up of both carbonate and quartz clasts. There, shear deformation was recorded by foliated mylonitic fabric dipping ca. 20° S, and by a well-developed, east-trending stretching lineation defined by aligned quartz or calcite grains. Conglomerates levels, when affected by shearing, were boudinaged within the mylonitic sandstones, and the individual elongated pebbles re-oriented along slip direction. The mylonitic foliation is nearly parallel to the tectonic contact between the Messinian sedimentary cover of the Apulian carbonates and the overlying allochton.

The microstructure of mylonites is characterized by a fine-grained calcite matrix, which shows an intense foliation defined by bands of dark material made up of oxides and organic matter with minor phyllosilicates. Subangular quartz grains, with a size of 0.1-0.3 mm, and a few rounded, cm-sized limestone clasts are embedded within the matrix. Quartz grains are fragmented by foliation-perpendicular, opening-mode fractures. Fragments, arranged in trails aligned to the foliation, show in some cases evidence of rotation due to the simple shear component of deformation. Altogether, shear bands, rootles folds and asymmetric porphyroclasts show a consistent top-to-the-east shear sense. Summing up, we may document that eastward movement of the allochtonous units of the Southern Apennines produced intense and localized low-temperature shearing in sediments on top of the Apulian platform. Further studies are required to confirm later reactivation of this shear zones as low-angle normal fault during the late Pliocene.

# The Variscan basament exposed in the southern Calabria: a Late Carboniferous network of shear zone?

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Keywords: shear zone, southern Calabria, Late Carboniferous.

The Calabria-Peloritani Orogen is a fragment that shows deformed sequences derived from the upper to the lower continental crust of the Variscan basament. The current geographic position derives from a migration of the Calabrian arc to the SE, which ended in the Miocene.

The study area is located in the south-east of the Serre Massif. The work focuses on the meso- and marcostructural analysis of two main tectonic units; the "Mammola Paragneiss Unit" (MPU) and the 'Stilo-Pazzano Phyllite Unit" (SPU).

These two Units recorded polyphase deformation and regional metamorphism during the Carboniferous and were later affected by contact metamorphism, caused by the intrusion of large granitic bodies during Late Carboniferous-Early Permian (300-290 Ma) (Festa *et alii*, (2018)).

Deformation is characterized by superposed folds and foliations leading to folding thick milonite levels. The aim of this work is to unravel the deformation and kinematic history of the two units and to assess the geometry and the kinematics of the shear deformation causing the development of thick milonites.

The geomtery and the kinematics of the flow of the unravelled shear zone will be discussed in the framework of the network of shear zones affecting the Variscan Basement in the mediterranean area during the Carbonifeorus.

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# Petrology and structural geology help elucidate the occurrence of tectonometamorphic discontinuities in central Nepal Himalaya

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Keywords: Himalaya, Pseudosection, AvPT method.

Major discontinuities within orogenic belts can be recognized using a number of different criteria: lithological, structural, metamorphic, isotopic, geochronological, among others. Combining more than one criterion together is envisaged in order to prevent biases and/or mistakes within rock packages characterized by similar features (e.g. comparable ages, lithologies, strain rates). Moreover, direct survey of discontinuities is often hampered by extensive quaternary cover.

A method for the relatively straightforward detection of such discontinuities was tested in central Nepal Himalaya. In the Rasuwa district, a detailed structural, lithological and petrological study of different transects allowed the characterization of the tectonostratigraphic architecture and constrained the P-T evolution of different units within the Lesser (LHS) and Greater (GHS) Himalayan Sequences.

The P-T evolution of selected metapelite samples was constrained using two independent methods: optimal thermobarometry (i.e. Average PT - AvPT) and the pseudosection approach. P-T conditions independently constrained using the pseudosection approach plot very close to, or totally within the uncertainties of, the AvPT results. Peak P-T conditions obtained highlight the existence of four different T/P ratio populations in different tectonometamorphic units:  $80 \pm 11$  °C/kbar (LHS),  $66 \pm 7$  °C/kbar (Ramgarh Thrust Sheet: RTS),  $73 \pm 1$  °C/kbar (Lower-GHS) and  $101 \pm 12$  °C/kbar (Upper-GHS).

Integration of structural and petrological data emphasizes the existence of three tectonometamorphic discontinuities bounding these units, characterized by top-to-the-south sense of shear: the Ramgarh Thrust, which separates the LHS (peak metamorphism at ~600 °C, 7.5 kbar) from the overlying RTS (peak metamorphism at ~635 °C, 10 kbar); the Main Central Thrust, which separates the RTS from the Lower-GHS (peak at 700-740 °C, 9.5-10.5 kbar with a prograde increase in both P and T in the kyanite stability field), and the Langtang Thrust, which juxtaposes the Upper-GHS (peak at 780-800 °C, 7.5-8.0 kbar with a nearly isobaric heating in the sillimanite stability field) onto the Lower-GHS. An increase in the intensity of deformation, with development of pervasive mylonitic fabrics and/or shear zones, is generally observed approaching the discontinuities from either sides.

Our results demonstrate that petrological and structural analysis combined together, are reliable methods adequate to identify tectonometamorphic discontinuities in both the LHS and GHS.

Moreover, tectonometamorphic discontinuities may be detected using the relatively fast AvPT approach, which allows application of relative thermobarometry on a large number of samples, as an alternative to more laborious, time consuming, expensive, and complex, studies (e.g. pseudosections, geochronology, etc.) which could be exploited on specific and selected areas only.

### Identification of Mesozoic detachments preserved in the South Alpine basement (northern Como lake area, Italy)

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Keywords: Structural geology, Petrology, Passive margins.

A polyphase metamorphic basement crops out in the northern part of the South Alpine domain of the Alps (Spalla *et al.*, 2000). It is involved in Alpine tectonics and locally overprinted by low-grade Alpine metamorphism (Crespi et *al.*, 1982). Pre-Alpine and Alpine events must be distinguished in order to reconstruct the tectonic evolution. We investigated Pre-Alpine structures in the basement of the northern Lago di Como area with the aim to identify rift-related faults.

The well-known Lugano Val Grande Fault (LVGF) has been taken as example in order to identify other detachments preserved in the studied area (Bertotti 1991, Bertotti *et al.*, 1993). We investigated the tectonic contacts between Triassic carbonates and the Variscan basement in the Domaso-Cortafo Zone, south of the Insubric line. We identify for the first time the Sasso Pelo Detachment (SPD), forming the base of the Triassic succession and characterized by the superposition of carbonatic breccias without basement clasts above basement mylonite. The SPD displays the same structural characteristics as the LVGF, partitioning of the deformation mechanism along the fault zone, *i.e.* brittle structures in the hanging wall and ductile deformation in the footwall. Mylonites are found only in the footwall, both in micaschists and paragneisses. Cataclasites occur only in the hanging wall, at the base of the sedimentary breccias. The fault likely accommodated a large displacement because we find the juxtaposition of brecciated sedimentary rock directly above the mylonitic basement, as observed for the LVGF. The sense of transport along the SPD is top-to-the-West, opposite to the more southerly located LVGF (top-to-the-East). This may reflect a lateral polarity change in Mesozoic rift architecture, or, alternatively, a significant Alpine displacement along the Musso Line, a steep fault between the two detachments.

Our results demonstrate the occurrence of major pre-Alpine, post-Variscan crustal detachments. They were folded during the Alpine orogeny and partly eroded but are generally well preserved.

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## A mini-atlas of shear-related microstructures in late Variscan granitoid rock from the northeastern Peloritani Mountains (southern Italy)

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Keywords: Non-coaxial deformation, Variscan shear zones, NE Sicily.

The Peloritani Mountains, in NE Sicily, are the southern termination of the Calabria-Peloritani Orogen (CPO), a poly-orogenic basement made up of remnants of Variscan and older mountain chains, incorporated into the Alpine-Apennine orogenic system. Alpine shear zones are well known and documented in the peloritanian area (Cirrincione et al., 2015), whereas Variscan shear zone activity has been only tentatively suggested by Fiannacca et al. (2012). Late Variscan granitoid rocks of trondhjemitic and granitic composition make up small plutonic complexes (<20 km<sup>2</sup>), intruded in migmatitic paragneisses, in the north-eastern Peloritani. All the granitoids exhibit a range of deformation microstructures developed under simple-shear regime at various temperature conditions. Non-coaxial deformation is documented by sigmoidal feldspar porphyroclasts and polymineral aggregates, mica fish and asymmetric boudins developed in muscovite and tiny andalusite crystals. Evidence for possible late Variscan shearing affecting the cooling granitoid bodies is provided by diffuse chessboard pattern in quartz, which is considered to indicate high-temperature deformation, at more than 650 °C (Kruhl, 1996). Deformation developed at sub-magmatic conditions is extensively superposed by deformation at lower temperatures. Examples of solid state-high temperature deformation-related microstructures (>450°C) are represented by quartz grain boundary migration recrystallization, quartz ribbon and core-and-mantle structures of white mica. Widespread low temperature subsolidus microstructures (<450 °C) consist of bulging, subgrain rotation recrystallization, mica kinks and feldspar bending. Occurrence of quartz chessboard pattern in granitoids with emplacement ages ranging from c. 310 to c. 300 Ma reinforces the idea that high temperature deformation occurred during cooling of magmatic bodies rather than during Alpine metamorphism at prolonged upper amphibolite facies conditions.

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Keywords: Argentera Massif, Aiguilles Rouges Massif, East Variscan Shear Zone.

Recent models of the Southern European Variscan Belt propose the existence of a regional-scale rightlateral strike-slip fault known in the literature as East Variscan Shear Zone (EVSZ, Matte 2001; Corsini and Rolland 2009). Despite this sector of the Belt was fragmented and reworked during the subsequent Alpine Orogenesis, several evidences of the activity of the EVSZ are reported in the Sardinian Variscan Basement where the well-known Posada-Asinara Shear Zone is interpreted as the southern branch of the EVSZ (Carosi and Palmeri 2002; Carosi et al. 2012). Toward the north the evidence and the extension of the EVSZ are less clear. In the Western Alps recent studies of the Ferriere-Mollières shear zone (Argentera External Crystalline Massif; Simonetti et al., 2018) revealed that it is a Variscan shear zone developed during similar metamorphic conditions as the PAL in northern Sardinia at nearly the same time and with the same kinematics. This data suggests that the EVSZ extended to the north affecting the Alpine External Crystalline Massifs. In order to strenght this model we performed a new study on the structural asset, the kinematic of the flow, the finite strain and the geochronology of a high-strain zone in the Aiguilles Rouges Massif located between the Lake Emosson and the Val Berard area close to the boundary between Swiss and France. The results higlights a dextral pureshear dominated transpression developed under amphibolite-facies metamorphic conditions during Variscan time. The structural asset of the Lake Emosson-Val Berard shear zone is very similar to the one recognized for the Ferriere-Mollières shear zone in the Argentera Massif and they represent two well-preserved segments of the EVSZ. Further studies of other high-strain zones in the Alpine External Crystalline Massifs are needed to verify how much this sector of the Variscan chain was interested by the EVSZ.

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### Syn-shearing Mobility of Major Elements in Ductile Shear Zones: State Of The Art for Felsic Deformed Protoliths

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Keywords: Ductile shear zones, felsic rocks, fluid-rock interaction.

The mineralogy of ductilely sheared rocks is controlled by the bulk rock composition of the protolith, together with the P-T conditions of shearing. However, the mineral assemblages of shear zones acting as open system may be strongly influenced by the occurrence of mass transfer processes induced by channeling  $H_2O$ -rich fluids and mobilizing major elements. Major element mobility is also related to the fluid chemistry, which can be affected by the fluid source location, i.e. the shear zone host-rocks or the shear zone far-field. Recent case studies suggest that significant whole rock compositional changes occurred within ductile shear zones in response to fluid infiltration from the host-rocks, whereas other case studies show that whole rock compositional changes within ductile shear zones occurred due to infiltration of fluids from far-field sources. To investigate the presence of common features regarding the gain and loss of mobilized major elements with respect to the thermobaric conditions of shearing and the fluid source, a review of literature case studies dealing with felsic sheared protoliths has been undertaken.

Qualitative results suggest high mobility of major elements under greenschist facies conditions whatever the tectonic context. Under compressive tectonics, qualitative outcomes show that Si has the highest mobility whatever the fluid source location and that sheared felsic rocks are always enriched in Mg relative to Fe. Moreover, a preferential gain of Al and Fe with respect to the fluid source is shown.

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Keywords: Precambrian shear zones, Sveconorwegian orogen, Structural reactivation.

Due to their old age, Precambrian deformation zones are likely to have been reactivated multiple times after their nucleation. The mechanic weakness inherited from their earliest deformation thus becomes an important intrinsic property of the deforming system as it steers the deformation zones' subsequent geometric, kinematic and mechanic evolution. We discuss here the the tectonic evolution during the Meso- to Neoproterozoic Sveconorwegian orogeny (c. 1140-900 Ma) of the boundary zone between the Kongsberg and Telemark lithotectonic units in S Norway, referred to as the Kongsberg-Telemark Boundary Zone (KTBZ). The orogenscale KTBZ developed predominantly within and at the margin of a c. 110 km long granitic belt intruded between 1170 and 1146 The oldest KTBZ ductile fabric formed during the Sveconorwegian orogenic cycle as a penetrative top-to-the-W shear fabric, which was subsequently reactivated selectively by sinistral transpression that formed characteristic mylonitic shear zones within the granitic belt. Later folding affected the area at the northern end of the Kongsberg lithotectonic unit. All these structures are cut by late-Sveconorwegian, E-dipping shear zones and normal faults, which accommodated a distinct phase of exhumation of the Telemark lithotectonic unit in the footwall of the KTBZ. This extensional detachment, fully constrained by Ar-Ar geochronological results, widens toward the north, where it might have controlled the emplacement of volumetrically consipcuous late-orogenic granites. Since late Sveconorwegian times, the KTBZ was repeatedly reactivated in a brittle fashion forming complex fault patterns, extensive quartz vein networks and leading to the generation of the socalled "Store Rivnings-breksje", a 100 km long brittle fault zone that follows the trend of the KTBZ and that locally juxtaposes blocks with different ductile precursor histories. The newly established deformation history helps to refine existing models for the orogenic evolution of the central Syeconorwegian orogen. The reactivation history established for the KTBZ helps to better understand the dynamics of long-lived weakness zones of Precambrian origin in general. The intrinsic mechanic weakness of reactivated shear zones plays a significant role in the process of terrane amalgamation, wherein comparatively less deformed crustal units are juxtaposed along narrow and long-lived, high-strain domains that shape the first-order architecture of orogens. Reactivation at the large scale, however, can be transient and very selective reflecting the orientation of the inherited fabrics with regard to the active stress field plays. Geological studies dealing with the geometric, kinematic and temporal evolution of old deformation zones should therefore not be based on a few, scattered observations from a limited number of outcrops. They should instead be as comprehensive as possible and rely on large datasets and on a well-integrated multi-disciplinary approach.

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#### Deformation microstructures and processes in serpentinites: from weak to ultraweak behavior

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Keywords: Retrograde serpentinite, slickenfibers veins, (001) sliding.

Serpentinites play a key role in controlling fault rheology in a wide range of geodynamic settings, from oceanic and continental rift zones to subduction zones. In particular, lizardite + chrysotile retrograde serpentinites are considered as relatively weak rocks, possibly accounting for the aseismic creeping behavior of fault zones in the oceanic and continental lithosphere. However, the frictional strength of serpentinites is still debated, partly because previous experimental measurements of the friction coefficient of different serpentine samples do not reveal a consistent picture. In this study, we report detailed micro/nanostructural and mineralogical observations of retrograde serpentinites during progressive deformation, combined with determinations of the friction coefficient  $\mu$  for well constrained samples.

Massive retrograde serpentinites show an evolution from undeformed mesh and bastite pseudomorphic textures ( $\mu = 0.3$ ) to foliated, ribbon-like textures formed by lizardite with strong crystallographic and shape preferred orientations ( $\mu = 0.18$ ). Overall observations indicate that pressure solution and  $(001)_{iiz}$  frictional sliding are the most important deformation mechanisms in massive retrograde serpentinite. We also discuss the possible mechanical significance of fibrous serpentine veins, that typically occur in all serpentinite outcrops and represent the main products of pressure solution and re-precipitation processes. Fibrous veins ( $\mu = 0.15$ ) typically form a complex system of anastomosing and interconnected slickenfiber faults. Therefore, the occurrence of both lizardite-rich foliated serpentinites and fibrous slickenfiber veins/faults may collectively lead to progressive and substantial weakening of the shear zone, with further reduction of the friction coefficient from  $\mu = 0.3$  to  $\mu = 0.15$ .

# Session S11 Tectono-metamorphic processes from micro-scale to plate margins: Geological, Geophysical and Petrological approaches in unravelling the evolution of metamorphic terrains in collisional belts

Conveners AND CHAIRPERSONS Gaetano Ortolano (Università di Catania) Annamaria Marotta (Università di Milano) Maria Iole Spalla (Università di Milano)

# Relations between induced birefringence haloes and polarized raman spectra in host cubic crystals

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Keywords: mineral inclusions, cubic crystals, birefringent halo.

Raman measurements to investigate the elastic response of inclusions trapped in their host for geobarometric applications are under extensive development. However, while controversial issues related to the application of elastic barometry to non-ideal cases have been addressed (e.g., Mazzucchelli et al., 2018), the strain state in the host mineral has never been shown and discussed in detail. Often cubic crystals, such as garnet, show birefringent haloes around strained inclusions, but the direct relationship between this feature and the Raman spectra has not been found yet. While most authors aim at determining the strain in the host adjacent an inclusion by means of the Raman peak position with respect to a free crystal (e.g., Izraeli et al., 1999), we propose, for cubic crystals, the change in the depolarization ratio of total symmetric phonon modes as a new method. Indeed, Raman peak positions are related to the nuclear equilibrium configuration of a crystal, whereas Raman peak intensities are related to the polarizability of the electron shells. Therefore, since electrons are "lighter", they can be much more sensitive to small stress fields induced by the inclusion-host contact surface. Using this approach, we found a direct correlation between the induced birefringent halo and the intensities of Raman peaks in polarized spectra of the host. Therefore, we present the first experimental evidence of lattice shear strain induced by the presence of "pressurized" inclusions on the host, without any variation in the peak positions of its Raman spectrum.

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### A geological map of the Liguride complex of the Pollino area (Southern Apennines)

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Keywords: Geological Map, Liguride Complex, Southern Apennines.

The calabro-lucanian sector of the southern Apennines includes the major paleogeographic domains derived from the Alpine Tethys and the Adria plate. Therefore, it is a key area for understanding the geodynamic evolution of western-central Mediterranean. Our study shows the results of detailed geological-structural mapping as well as minero-petrographic, petrological and preliminary calcareous nannofossils biostratigraphic studies aimed at reconstructing the tectono-stratigraphic relationships among different units of the Liguride Complex. Four major tectonic units, characterized by an overall decrease of metamorphic grade from top to bottom, have been identified: i) slices of continental crust rocks consisting of Albitic gneisses, Garnet gneisses and Amphibolites; ii) the Frido Unit; iii) the Seluci-Cogliandrino Unit and iv) the Nord Calabrian Unit. The base of the Frido Unit consists of serpentinites, foliated metabasites and the M. Nandiniello Metalimestones, frequently occurring in an overturned succession. In the western sector, metabreccias and metarenites occur between metabasites and the M. Nandiniello Metalimestones. In the northern sector, a typical seafloor sequence is recognized. The upper part of the Frido Unit consists of gray slates with intercalations of fine-grained, greygreen metalimestones and quarzites, with phyllosilicates indicating HP/LT metamorphic conditions. This is in agreement with the presence of carpholite and aragonite in the metasediments as well as with the occurrence of glaucophane and lawsonite in the metabasites. The Seluci-Cogliandrino Unit consists mostly of metapelites characterized by a main foliation and incipient crenulations. Data on phyllosilicates from this unit suggest P-T conditions intermediate between the Frido and the Nord Calabrian Unit. This latter is represented, from the bottom, by the Timpa delle Murge Ophiolites, radiolarites and shales of the Timpa delle Murge Fm., the Crete Nere and Saraceno Fms, covered by the thrust top deposits of the Albidona Fm. Phyllosilicates of the Crete Nere and Saraceno Fms constrain P-T conditions at the lower part of high diagenesis.

Biostratigraphic results show that the Frido Unit did not preserve any calcareous nannofossil because of strong deformation and metamorphic recrystallization. In the North Calabrian Unit, the Crete Nere Fm was found barren, while late Albian ages were documented in the lower part of the Saraceno Fm. by the occurrence of *Eiffellithus turriseiffelii* and *Hayesites irregularis*. Accordingly, in the basal part of the Albidona Fm, the occurrence of *Discoaster lodoensis, Reticulofenestra dictyoda* and *Toweius callosus* testify the uppermost early Eocene. These preliminary data clearly indicate that a more in-depth biostratigraphic study would provide essential information for constraining the geodynamic reconstruction of the Mediterranean area.

## Lithostratigraphic and structural features of the Monte Banchetta - Punta Rognosa massif (Western Alps, Italy)

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Keywords: Monte Banchetta-Punta Rognosa, Western Alps, geological setting.

The Monte Banchetta - Punta Rognosa massif is located between Troncea and Chisonetto valleys (Piemonte, Western Alps). It consists of a complex of oceanic and continental rocks, tectonically bounded by several oceanic units (Polino et al., in press and references therein). New structural, lithological and petrological studies of this area highlights the occurrence of three different successions, recording during the Mesozoic the tectono-depositional evolution of continental, proximal and oceanic sectors. The continental crust succession consists of a composite pre-Triassic basement (?), overlaid by a Triassic to Lower Jurassic (?) sequence of quartzite, meta-dolostone and dolomitic meta-breccia, and calcschist in the upper part. The proximal succession is characterized by a Triassic (?)-Jurassic (?) heteropic sequence of polymictic meta-breccias (with dolostone and quartzite clasts), carbonate-bearing quartzite and quartzite containing dolostone clasts, wrapped by black shales. The oceanic succession is composed of serpentinite with ophicarbonate, overlaid by heterogeneous meta-breccia with both oceanic and continental-derived clasts, followed up section by discontinuous levels of impure quarzite, locally containing thin layers of para-metabasite and plurimetric dolomitic olistoliths. Both the oceanic succession and the proximal succession are stratigraphically overlaid by calcschist, locally containing levels of green and black shales and scarce bodies of various meta-ophiolite (upper Jurassic?-Cretaceous?). The three successions generally show an Alpine metamorphism from HP-LT (blue-schist facies) to LP-LT (green-schist facies) conditions. Four folding phases have been recognized: both the first (D1) and the second (D2) deformation phases are recorded by non-cylindrical folds associated to pervasive axial plane schistosities. The third phase (D3) determined a small-scale crenulation cleavage and large-scale folds with generally sub-horizontal ENE-WSW trending axes and axial planes dipping to S at high angle. The fourth phase (D4) consists of gentle folds with N-S trending axis and high-angle axial plane. Contacts among rocks of the identified successions are determined by polyphasic shear zones related to D1, D2 and D3 phases, showing often evidences of late extensional reactivation. Folds and shear structures are cut by high-angle normal to transtensive fault systems, mainly NE-SW, N-S and NNW-SSE- trending.

Polino R., Fioraso G., Malusà M., Mosca P. (in press): Carta Geologica d'Italia alla scala 1:50.000. Foglio 171 "Cesana Torinese". Serv. Geol. It., Roma. (<u>http://www.isprambiente.gov.it</u>).

### Quantitative analysis of metamorphic reaction progress along strain gradients in granitoid and basic rocks from Lago della Vecchia, Sesia-Lanzo Zone, Western Alps

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Keywords: Q-XRMA, min-GSD, tectono-metamorphic evolution.

The quantification of the actual rock volumes in which metamorphic transformations progress is a key to investigate the complex interactions of mineral chemical and phase changes during heterogeneous deformation development. Recognizing homogeneous metamorphic domains for each re-equilibration stage is the basis for reconstructing the tectono-metamorphic evolution via analysis of structural and petrologic overprints.

The Sesia Lanzo Zone (SLZ) belongs to the Austroalpine domain of the Western Alps and is interpreted as a slice of the Adria continental margin involved in the Alpine subduction and collision. The SLZ experienced eclogite facies conditions, followed by a re-equilibration under blueschist conditions compatible with an exhumation accomplished during the subduction of oceanic lithosphere. Afterwards, it was partially affected by a greenschist facies event, associated with the exhumation to the uppermost part of the tertiary nappe stack. The study area (Lago della Vecchia) is located within the central SLZ.

To investigate the textural and chemical heterogeneities developed during Alpine deformation and metamorphism partitioning, we used two ArcGis-based tools: (i) Q-XRMA creates polygons that represent mineral phases, quantifies the modal mineral percentage, and the element concentrations of selected mineral phases by calibrating the X-ray maps with mineral chemical analysis used as internal standard; (ii) min-GSD allows the quantitative analysis of the grain size distribution of different phases combing the optical scans, the vectorization of the scans, and the Q-XRMA mineral classification.

Here we show the results for a coronitic metagranitoid and mylonitic metabasite samples, with a dominant blueschist imprint and igneous and eclogitic mineral relicts. For both samples we applied both methods to the entire thin-section and to crucial microdomains.

Metagranitoid sample displays different D2 coronae of fine-grained mineral associations (Grt+Bt+Wm+Pl) that depend on the igneous microdomains replaced. The analyses focus on the continuous and composite corona of Grt+Wm+Bt+Pl developed between igneous Bt and Pl domains. In particular, Grt displays an Mn-reach core and asymmetrical rim zonation that consists of Mg and Ca enrichment towards Bt and Pl domains, respectively. The metabasite sample analysis is in progress and it focuses on the calibration of garnet, pyroxene, and white mica to quantify the spatial distribution of the successive generation of these phases to be related with chemical variations in relation to D1 and D2 stages. These petrological and chemical results allow more accurate individuation of microdomains in chemical and textural equilibrium for more reliable thermobarometric estimations of D1 and D2 tectono-metamorphic stages and better estimation of degree of metamorphic reaction progress along strain gradients.

### Geochemical data on the Ordovician magmatism of Sardinia Variscan chain: the case study of Monte Filau orthogneiss

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Keywords: geochemistry, SW Sardinia, Ordovician magmatism.

The Mt. Filau orthogneiss is an Ordovician orthogneiss outcropping in the External Zone of SW Sardinia chain. It consists of (i) a dark, biotite-rich facies, (ii) a leucocratic coarse-grained facies and (iii) a leucocratic fine-grained facies. Biotite-bearing orthogneiss is a coarse-grained, inequigranular, foliated gneiss, consisting of quartz, K-feldspar, plagioclase, and minor amounts of muscovite and biotite. Accessory phases are zircon, monazite, apatite and Ti-Fe oxides. Rare garnet, andalusite and tourmaline have been found. Coarse-grained, leucocratic orthogneiss is biotite-free and shows higher muscovite content as compared to the biotite-bearing ones. Fine-grained, leucocratic orthogneiss is quite different. The average grain size is commonly lower than 0.2 mm, and the foliation is less marked due to the lower amount of white mica and granoblastic fabric in quartz-feldspar layers. Coarse-grained andalusite (1-3 vol.%) is up to 0.5 mm in size. Muscovite is found as coarse-grained crystals (up to several millimeters) with andalusite and rounded quartz inclusions and rarely hosting sillimanite needles. Coarse- and fine-grained leucocratic orthogneisses are slightly enriched in SiO, and depleted in Fe<sub>2</sub>O<sub>2</sub>, MgO, TiO<sub>2</sub> and CaO as compared to the biotite-bearing orthogneiss. This latter shows higher Sr and Ba concentrations than leucocratic ones, whereas Rb content is higher in leucocratic orthogneiss as compared to the biotite-bearing ones. All the three facies of the Mt. Filau orthogneiss show the typical signature of calcalkaline rocks, with negative anomalies of Ba, Nb, Sr and Ti, and positive anomalies in U, K. REE patterns of biotite-bearing and coarse-grained leucocratic orthogneisses are characterized by a moderate LREE fractionation, flat HREE and negative Eu anomaly. Fine-grained leucocratic orthogneiss shows flatter patterns, stronger Eu anomalies and slight HREE enrichment. Selected trace and REE elements of Mt. Filau are compared with other Ordovician orthogneiss outcropping in the Axial Zone of Sardinia Variscan belt. The geochemical affinity of orthogneisses and metavolcanics from Variscan Sardinia, together with the geochronological data, allows to state a clear cogenetic relationship between the igneous bodies belonging to the calcalkaline Ordovician magmatic cycle. Our results suggest that the early Paleozoic basement of Sardinia might represent the witness of an early Paleozoic subduction-accretionary complex recording convergence along the northern Gondwana margin.

## Metamorphic evolution of the Saka Unit (Central Pontides, Northern Turkey): new implications for the Mesozoic convergence-related processes in the Intra-Pontide suture zone

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Keywords: Metamorphic Evolution, Saka Unit, Intra-Pontide Suture Zone.

In Northern Turkey, the Intra-Pontide suture (IPS) zone represents an east-west trending belt of deformed and/or metamorphic rocks bounded by the Istanbul-Zonguldak Terrane (IZ) to the north and the Sakarya Composite Terrane (SK) to the south (e.g. Göncüoğlu et al., 1997). Despite its importance for the geodynamics reconstructions of the Black Sea and Eastern Mediterranean areas during the Mesozoic, the IPS zone has been poorly investigated; only recently the role of its metamorphic units during the syn-collisional evolution was explored (Marroni et al., 2014; Frassi et al., 2016; 2017)

In order to provide new insights on the Mesozoic-Tertiary geodynamic reconstruction of the southern margin of the Laurasia, we present new data from the Saka Unit from the eastern portion of the IPS. Using a multidisciplinary approach that includes lithological, structural, metamorphic and petrographic investigations, we constrained the P-T-t path during the Mesozoic subduction and consequent exhumation and accretion to Laurasia. Following the determination of mesostructures, we analysed a series of samples of metabasite and metapelite. Mineral chemistry of phases at equilibrium in the pervasive S2 foliation was determined, and PT determinations were performed through pseudosection calculation of three samples. PT conditions are within the epidote-amphibolite facies, with pressures of  $1.2 \pm 0.15$  GPa and Temperatures  $600 \pm 50$  °C, thus higher than those determined previously, suggesting that S2 could be a composite foliation where a progressive evolution acquired during onset of exhumation was recorded. A comparison with the PT evolutions of the nearby Daday and Domuz-Dag units, shows that they record lower T at D2 at different ages, and that the pre-D2 conditions, when they are preserved, are different in the three units.

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#### Raman vs. classic geothermobarometry: a comparative study

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Keywords: Raman geobarometry, geothermobarometry.

The precise characterization of the PT(t) histories of subducted rocks is of key importance in metamorphic geology. An accurate (or inaccurate) PT and depth estimate might have strong implication on the interpretation of other PT-dependent processes, like geochemistry of subduction zone fluids, the element recycling and transfer to volcanic arcs and the interpretation of geophysical imaging of modern-day convergent margins.

The most used and accessible empirical methods for estimating PT equilibration conditions are 1) elementexchange geothermobarometry, 2) thermodynamic modelling and 3) Raman barometry. These three methods are generally well calibrated and consistent within their experimental error. However, one main limitation is given by the assumption of thermodynamic equilibrium between the phases and of hydrostatic equilibration pressure. This latter assumption therefore excludes the possibility of non-lithostatic stresses build up at the grain or sub-grain scale. Angel et al. (2015) and Murri et al. (in press) have shown that the Raman spectroscopy of a host-inclusion system provides information on its stress state.

However, the magnitude of discrepancies between Raman and classic geothermobarometry is still unknown. Following the approach by Murri et al. (in press), we performed a comparative study between classical element-exchange geothermobarometric methods, thermodynamic modelling and Raman geobarometry on a garnet-kyanite gneiss and a quartz-garnet vein from the Fjørtoft UHP terrane, Norway. Preliminary results will be presented.

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Angel, R.J., Nimis, P., Mazzucchelli, M.L., Alvaro, M., Nestola, F. (2015): How large are departures from lithostatic pressure? Constraints from host-inclusion elasticity. Journal of Metamorphic Geology, 33, 801-813.

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### Estimating differences in peak P-T conditions in the (U)HP tectonic nappe stack of Southern Dora-Maira Massif (Western Alps)

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Keywords: (U)HP metamorphism, peak P-T conditions, thermobarometry.

The first discovery, more than 30 years ago, of coesite in the Brossasco Isasca Unit (BIU) of the southern Dora-Maira Massif, western Alps, demonstrated the possibility for continental crust to reach ultra-high pressure (UHP) conditions. However, the geodynamic processes responsible for the formation and exhumation of continental UHP units are still debated. Conceptual and numerical models that try to explain how a continental unit is exhumed from UHP conditions are calibrated against existing geological and petrological data from the tectonic nappe stack which includes the UHP unit itself. A precise knowledge of peak P-T conditions experienced by both the UHP unit and its adjacent units is therefore the crucial starting point to test the validity of the models.

In the southern Dora-Maira Massif, the UHP BIU is structurally sandwiched between two quartz-eclogite facies units, the lower San Chiaffredo Unit (SCU) and the upper Rocca Solei Unit (RSU), which are in turn bounded by two blueschist-facies units, the Pinerolo Unit (PU) at the bottom and the Dronero Unit (DU) at the top of the tectonometamorphic package. In contrast to the well constrained P-T evolution of the BIU (peak P-T conditions at 730°C, 40 kbar), peak P-T conditions for its adjacent units are poorly constrained, most studies dating back to more than 15 years ago and mostly relying on conventional thermobarometric methods.

This contribution provides, for the first time, a precise estimate of the peak P-T conditions registered by the HP units bounding the BIU, using the same (internally consistent and therefore comparable) modern thermobarometric approaches. The study focuses on metapelites (garnet-bearing phengitic micaschists), which are among the most common lithologies in all the investigated units, and well preserve the (U)HP assemblages. Five metapelites, one for each unit (PU, SCU, BIU, RSU, DU), are studied in detail. Thermobarometric estimates are obtained combining multi-equilibrium thermobarometry (Average PT) and the pseudosection approach, and considering the effects of chemical fractionation of the bulk rock composition, as well as the influence of the oxidation state.

The obtained results show that: (i) the UHP BIU is sandwiched within imbricate thrust sheets which show substantial P-T gaps; (ii) peak P-T conditions estimated for the units underlying and overlying the BIU are more scattered than previously thought and define significantly lower T/P gradients; (iii) near-UHP peak conditions, at T significantly lower than those of the BIU, are suggested for the RSU. These new data represent the inescapable starting point for any model aimed to a deeper understanding of the subduction/exhumation processes of UHP continental units.

## Structural-geological survey of an eclogitized chaotic complex: the Riffelberg - Garten Unit in the Breuil dell (Zermatt-Saas Zone, Italian Western Alps)

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Keywords: Integrated structural and petrologic analysis, Alpine subduction, polygenetic mélange.

The Riffelberg-Garten Unit (RGU) is a tectono-stratigraphic unit, belonging to the Zermatt-Saas Zone (ZSZ), characterized by a chaotic mixture of metasediments, metabasites and serpentinites (Bearth, 1967; Dal Piaz & Ernst, 1978; Campari et al., 2004). In particular the RGU is composed by meter to cm-sized clasts of eclogites, glaucophanites, marbles, and serpentinites within a heterogenous matrix of micaschists, marbles and calcschists. This unit mainly occurs in the Valais and in upper Aosta Valley, and its originally complex lithostratigraphy is further complicated by polyphase deformation generated during Alpine subduction, collision, and the subsequent exhumation. Such a complexity makes the origin of this mélange still debated. The multiscale structural analysis was performed over an area of 12km<sup>2</sup> in the upper Valtournanche valley (Breuil) and revealed the occurrence of four superposed groups of ductile structures. The new structural map at 1:5000 scale has been integrated by form surface maps performed at more detailed scales (1:100, 1:50, 1:200). Microstructural and petrologic investigations show that the first two groups of structures, D1 and D2, developed under eclogite facies conditions, while D3 and D4 developed under decreasing P and T during the progressive RGU exhumation. New quantitative PT estimates suggest that the thermal regime associated with the development of D1 and D2 structures is compatible with a cold subduction, as the one already inferred for ZSZ. On the contrary the T/P ratio characterizing D3 and D4 results to be higher, indicating that the exhumation occurred in a mature collisional setting.

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## Integrating geological data with numerical models for the understanding of the Ross-Delamerian Orogeny in northern Victoria Land (Antarctica)

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Keywords: paleo-Pacific Gondwana evolution, northern Victoria Land, 2D numerical models.

The basement of the northern Victoria Land (nVL, section of the Transantarctic Mountains, Antarctica) mostly consists of Neo-Proterozoic to Early Paleozoic lithotectonic units derived from subduction processes at the paleo-Pacific continental margin of Gondwana during the Ross-Delamerian Orogeny.

Up to now, several scenarios have been proposed to explain the geodynamic setting of the paleo-Pacific Gondwana continental margin in this sector, involving (i) exotic or local provenances of terranes that amalgamated or accreted at the margin, (ii) either one (or more) continuous southwest dipping subduction zone(s) or (iii) changing polarities of subduction zones with time.

While there is general agreement on the subduction-related tectonic setting in nVL in the Late Neo-Proterozoic to Early Paleozoic, the different geodynamic frameworks are still heavily debated in the recent literature. The different scenarios involve:

a) one southwest-directed subduction zone of the palaeo-Pacific Ocean under the East Gondwana active continental margin, involving the opening of a back-arc basin between two volcanic arcs;

b) a main westward subduction and local, transient subduction zones related to a boudinaged and stretched forearc after slab roll-back and trench retreat, with the opening of one or more marginal and back-arc basins; in this case, the magmatic arcs migrate first towards the ocean and later towards the continent;

c) a double (limited in time) west-ward directed subduction zone evolving in an island arc-continental arc collision;

d) an eastward directed subduction zone, which flipped into a westward subduction after fore-arc/arc-continent collision; the collision drove further igneous activity in the newly accreted terranes producing an Andean-style magmatic arc on continental crust.

In this study, we combine geological data derived from the literature, integrated by new investigations, and 2D numerical models simulating a subduction process in order to give further constraints on the geodynamic evolution of the Ross-Delamerian Orogeny in nVL.

The employed numerical code solves thermo-mechanical equations with finite differences method and marker-in-cell techniques, combined with a multigrid approach. We first considered an ocean-continent subduction with the oceanic plate topped by a Pacific-style oceanic crust that counts for layers of gabbro, basalt and pelagic sediments; sediments cover also the continental margin. In all model runs, we particularly analyze among others the birth and disruption of volcanic arcs, their location according to the distance of the subduction initiation point from the continental margin and to the initial inclination of the subducting slab, and the formation and evolution of extensional basins.

### Elastic geobarometry for elastically anisotropic inclusions

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Keywords: deviatoric stress, elastic anisotropy, mineral inclusions.

Mineral inclusions entrapped in other minerals may record the local stresses at the moment of the entrapment in deep portions of the Earth that we cannot access directly. When rocks are exhumed to the surface of the Earth, residual stresses and strains may be still preserved in the inclusion. If measured and interpreted correctly through elastic geobarometry, they give us invaluable information on the pressures and temperature of metamorphism during geodynamical processes such as subduction. Current estimates of P and T of entrapment rely on a simplified model that assumes that the inclusion is spherical and at the centre of an infinite host, and that the elastic properties of the host and of the inclusion are elastically isotropic. Recently, Mazzucchelli et al. (2018) showed that the real geometry of the system can be accounted for in calculations, keeping however the assumption of isotropic elasticity.

Here we report a new method for elastic geobarometry for spherical elastically anisotropic inclusions in quasi-isotropic hosts, based on a combination of equations of state and finite element modelling. This approach can be used to predict the residual strain/stress state in an inclusion if the entrapment conditions are known, or to estimate the entrapment conditions from the residual strain measured in real inclusions. Examples will be shown of applications to inclusions in pyrope garnet, which is almost elastically isotropic and a common host in ultra-high pressure metamorphic rocks. For a quartz inclusion entrapped in pyrope under lithostatic conditions during a prograde metamorphic path (2 GPa, 500 °C) we find that low differential stresses ( $\sigma_{max} - \sigma_{min} \approx 0.002$  GPa) should be expected in the inclusion at retrieval.

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### Raman elastic geobarometry for anisotropic mineral inclusions

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Keywords: deviatoric stress, elastic anisotropy, mineral inclusions.

Mineral inclusions entrapped in ultra-high-pressure metamorphic rocks can provide fundamental information about geological processes such as subduction and continental collision. When a host-inclusion pair is exhumed from depth to the Earth's surface non-lithostatic stresses are developed in the inclusion because of the contrast in their elastic properties (Angel et al., 2015). Elastic geobarometry for host-inclusion systems can be used to determine pressure and temperature conditions experienced by minerals during subduction or ultra-high-pressure metamorphism. However, current experimental approaches and theory are developed only for crystals immersed in a hydrostatic stress field whereas inclusions experience deviatoric stress.

Therefore, we have developed a method to determine the strains in quartz inclusions from Raman spectroscopy using the concept of the phonon-mode Grüneisen tensor (Ziman, 1960). We used *ab initio* Hartree-Fock/Density Functional Theory to calculate the wavenumbers of the Raman-active modes as a function of different strain conditions. Least-squares fits of the phonon-wavenumber shifts against strains have been used to obtain the components of the mode Grüneisen tensor of quartz ( $\gamma_1^m$  and  $\gamma_3^m$ ) that can be used to calculate the strains in inclusions directly from the measured Raman shifts. The concept is demonstrated with the example of a natural quartz inclusion in eclogitic garnet from the Mir kimberlite and has been validated against direct X-ray diffraction measurement of the strains in the same inclusion.

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# Tourmaline zoning pattern recording fluid evolution in the Kokchetav diamond grade metamorphic rocks

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Keywords: tourmaline, fluid, maruyamaite.

Due to its high compositional sensitivity and slow diffusion rate, tourmaline can record changes in bulk composition and help reconstructing metamorphic paths and fluid-rock interactions. Ota et al. (2008) and Shimizu & Ogasawara (2013) recently linked diamond-bearing high-K tourmaline (maruyamaite) to the UHP metamorphic peak in the Kokchetav massif. This finding arises question on the stability field of tourmaline and on the possible entrapment of diamonds in retrograde mineral phases.

In this work, we studied different species of tournalines from the UHP rocks from the Kumdy-Kol unit (Kokchetav Massif) for their compositional variations and inclusion mineralogy. Tournaline displays several different zoning-types: we identified the evolutional trend of tournalines from different rock types, according to their core-to-rim compositional zoning. While the composition of the tournaline core varies according to the bulk-rock chemistry, the composition of the rim is constant through the samples and presents an enrichment in Ca and Fe. Furthermore, the K content in tournaline is either maximum in the core, with a gradual or stepwise decrease toward the rims, or (ii) maximum in the mantle.

The distribution of mineral inclusions (diamond as a UHP indicator and quartz-graphite association as an indicator of low pressures) does not match the tournaline zoning. Several quartz inclusions in tournaline lack of coesite-to-quartz transformation microstructures and show the same Ti content as quartz in the matrix. Taking into account the presence of rutile in the bulk rock, we used the TinaniQ thermobarometer (Tomas et al., 2010) both for the bulk rock and quartz inclusions in the K-rich tournaline zones.

We will discuss the latest PT estimates for tourmaline crystallization and the environmental factors (changes in PT and/or fluid composition) controlling K incorporation in the tourmaline's structure.

This study was supported by the RSF grant 18-17-00186.

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# Garnet diffusion modelling applied for discovering timescales and rates of geological processes: two different case from Serre and Sila massifs (Calabria, Italy)

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Keywords: Diffusion modelling, Sila, Serre.

Deep tectono-metamorphic processes that driven the Earth orogenic dynamics can be very "fast", as suggested by the study of metamorphic rocks where mineral assemblages and compositionally-zoned crystals preserve the prograde growth history (*e.g.*, Zhang et al., 2010). However, long-lasting high-T processes can destroy the trace of the early *P*-T path, by erasing the original chemical zoning acquired by some minerals during their growth (*e.g.*, Spear, 2014).

In this context, diffusion modelling using the zoning of major elements is a valuable tool for outlining and quantifying how long a zoned mineral in chemical disequilibrium with the surrounding matrix can preserve its pre-existing composition and zoning, before being homogenised by diffusion mechanisms. A complete knowledge of how diffusion works in minerals, under different *P-T-X* conditions, becomes crucial in dealing with any attempt of tectono-metamorphic reconstruction based on the chemical compositions.

We present here two different diffusion models from two different case studies considered representative of different geological setting. The first one comes from the Serre Massif (Southern Calabria, Italy), located in the central portion of the Calabria-Peloritani Orogen. Almandine-rich mm-sized garnet crystals from several micaschist samples show relict inclusion-rich cores rimmed by inclusion-poor overgrowths. The second case study is from the Sila Massif (Northern Calabria, Italy) and, in particular, from a portion of the Calabria crystalline basement known in the literature as "Castagna Unit" (Dubois & Glangeaud, 1965). In this case, mm-sized almandine-rich garnet crystals from various mylonitic gneiss samples exhibit a "quasi"-absent crystal zoning.

The results, in particular of the first case study, show that the preserved growth zoning resulted from a rapid exhumation, able to maintain the original chemical patterns. In the second case, the flat zoning of the garnet core reflects a long residence at high temperatures before exhumation.

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# High pressure melting of eclogite: structural and geochemical evidence for multiple metasomatism of grt-peridotites from the Duria Area (Central Alps, N Italy)

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Keywords: Adula Nappe, Subduction, Mantle.

The Duria Area is located in the southern part of the Adula Nappe complex on the north-eastern side of the Como Lake (N Italy). Garnet/chlorite peridotites outcrop within migmatitic gneiss or in direct contact with amphibole-bearing migmatites containing boudins of variably granulitised eclogites. The contact between mafic and ultramafic rocks is marked by a metasomatic rim composed by tremolite and dispersed round-shaped chlorite aggregates, which also occurs within the peridotite body. The occurrence of lobes and cusps structures and Qtz+Pl+Kf+Bt leucosomes in eclogites provide evidence for partial melting of these rocks.

Petrography and mineral chemistry indicate that peridotites and associated eclogites experienced a HP metamorphic peak at  $\approx 2.8$  GPa and  $\approx 730 \pm 20$  °C, followed by a granulitic overprint at 0.8-1.2 GPa and 850 °C during their exhumation path (Tumiati et al. 2018).

The micostructural evidence of Qtz+Pl+Kf+Bt pockets in eclogites support the field evidence of a partial melting event. Eclogites are characterised by a HP assemblage formed by Grt+Ky+Omp+Kf, suggesting that a former phengite was completely consumed by the reaction Phe+Cpx+SiO<sub>2</sub>=Grt+Ky+Kfs+Melt. At this stage a clinopyroxenite reaction front probably results from a Ca-rich mafic silicate melt-peridotite interaction. Therefore, we suggest that tremolite-rich metasomatic rim probably represents a former grt-clinopyroxenite reaction front subsequently retrogressed at fluid-present conditions through the reaction Cpx+Opx+Grt+H<sub>2</sub>O=Tr+Chl.

Bulk rock trace element analyses of peridotites show a strong fractionation in REE (La/Nd<sub>N</sub>=2.4) likely indicating that these rocks record an interaction with a silicate melt. The metasomatic rim shows higher REE concentrations with a LREE enrichment and a slight Eu negative anomaly. This pattern broadly resembles the trace elements composition of pyroxenites from other localities of eastern Europe (i.e. Gföhl Moldanubian Nappe), interpreted as the product of infiltration of slab-derived melts in the overlying lithospheric wedge (Medaris et al., 2006). The trace elements patterns of peridotites, metasomatic rim, and associated eclogites show also an enrichment in fluid-mobile elements, such as Cs, Rb, Ba and K, and an high U/Th ratio suggesting that a subsequent fluid-assisted metasomatic event affected both mafic and ultramafic rocks under granulite or amphibolite facies conditions.

The Monte Duria area represents a unique case study where mafic melt-peridotite interaction occurs at high pressure and relatively high temperature in the Adula Nappe complex. The melt-rock interaction recorded by the Duria peridotites could thus represent a proxy for the crust-to mantle mass transfer at great depths in "warm" subduction environments.

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### The pre-Alpine polymetamorphic basement of the Southern Alps: A new petro-geochronological data set from the Dervio-Olgiasca Zone

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Keywords: Petrology, Geochronology, Rifting.

Situated, north of Como lake and south of the Insubric Line, the Dervio-Olgiasca Zone (DOZ, Bertotti et al., 1999; Spalla et al., 2000) belongs to the Southern Alps and provides ideal conditions to properly investigate the crustal pre-Alpine history due to the absence of Alpine metamorphism (Crespi *et al*, 1982).

The classical Variscan metamorphic sequence (Grt-St-Wm-Bt±Ky) has been partially recrystalised (Bt-Wm-Sil-Grt) during an early to middle Triassic LP-HT thermal event. A new set of petro-geochronological data with Lu/Hf on garnet and U-Pb and Th/Pb on monazite has been produced on pegmatite and micaschist. Such datable mineral texturally correlated with the tectono-metamorphic evolution of the schist allows to reconstruct the tectono-thermal stage of the Adriatic middle crust at the onset of the rifting.

Our study reveals an occurrence of a late Permo-Triassic thermal event (LP-HT) who induced a basement recrystallization only at the deepest structural level of the South Alpine crust. Afterward, because of the thermal cooling of the crust, lately greenschist overprint occurs also close to lithospheric scale extensional fault such as the well-know Lugano Val Grande Fault (LVGF). It overprints the Variscan paragenesis at shallow crustal levels (upper crust) and achieves the pre-alpine history of the basement.

Our results reveal that the Adriatic crust experienced local intense metamorphic events not related to Varsican or Alpine convergences, but to rifting processes related to the opening of the Tethyan ocean.

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# Phase equilibria for high-pressure serpentinites and compositionally-related rocks close to the MASH system

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Keywords: Thermodynamic modeling, thermocalc, ultramafic rocks.

Many poorly-studied rock compositions, such as metaserpentinite (Luoni et al., 2018; Rebay *et al.*, 2012; Rebay *et al.*, 2017), commonly record their PT evolution in quite remarkable detail. Using the current Holland & Powell dataset (Holland & Powell, 2011), and new activity-composition relations for antigorite and talc, calculated phase equilibria are presented for the essential "backbone" subsystem for many larger systems, MASH. Phase equilibria are also presented for departures from MASH, involving respectively FeO, CaO, and  $K_2O$ . The equilibria are applicable to serpentinites and some whiteschists and metapelites, for which some pseudosections and other phase diagrams illustrating phase relationships are used to highlight the role of composition and fluidavailability on the type of equilibrium assemblages preserved in such rocks in a wide range of PT conditions, mostly focussing on HP to UHP conditions.

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### Is the Rocca Canavese Thrust Sheet (Italian Western Alps) a subduction-related mélange? A multidisciplinary approach

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Keywords: Alpine subduction, Austroalpine Domain, multiscale petrostructural analysis.

In the Sesia-Lanzo Zone (SLZ), the subunit Rocca Canavese Thrust Sheet (RCT) is characterized by a mixture of mantle- and crust-derived lithologies such as metapelites, metagranitoids, metabasics, and serpentinised lherzolite lenses, from meter to hundred-meter size. We use a multidisciplinary approach in order to evaluate whether this tectonic mixture can be interpreted as a former subduction-related mélange in the Austroalpine domain. In particular, we perform a structural and metamorphic analysis of metagabbros, Jd-bearing and Lws-bearing glaucophanites to estimate their P-T-t-d evolution during the Alpine convergence. We also compare the geologic results with the predictions of a numerical simulation of an ocean-continent subduction zone.

Metagabbros and Jd-bearing glaucophanites experienced a D1a metamorphic stage characterized by a pressure of 1.3-1.8 GPa and temperature of 450-550°C, in eclogite facies condition. On the other hand, Lwsbearing glaucophanites experienced a D1b metamorphic stage at a temperature <470° and pressure of ca. 1.2-1.5 GPa, in Lws-blueschist facies condition. The two tectono-metamorphic units (TMUs) were coupled together during the exhumation at D2 stage, under Ep-blueschist facies conditions. Successive evolution occurs at lower pressure, under greenschist facies conditions. D1a peak conditions are compatible with a thermal gradient between a cold and a warm subduction zone, while D1b peak is recorded in a thermal gradient compatible with a cold subduction. The coupling between the two TMUs occurred under a cold thermal gradient, suggesting a still active subduction.

We develop a 2D FEM simulation of an ocean-continent subduction zone in order to verify the tectonic evolution of the two TMUs and estimate the amount of mixing occurring in a subduction-related mélange. The predictions of the numerical model well reproduce the two peak conditions (D1a and D1b) as well as the successive coupling of the two TMUs under Ep-blueschist facies conditions. Interesting, the peak conditions lie along two different P/T gradients. Thus, the two different thermal gradients showed by the two peak conditions can represent two burial paths probably accomplished in different positions within the subduction channel. The amount of mixing estimated in the field well agrees with that predicted by the numerical simulation. According to our multidisciplinary analysis, RCT is a tectonic mixture of recycled crustal slices and hydrated mantle material formed within a subduction channel. The different origin and P-T-d-t paths of the blocks, the intense shearing experienced by all lithologies during their coupling and the abundance of serpentinites in the tectonic mixture agree with the interpretation of a subduction-related mélange for RCT.

#### Geochronological constraints on the rates of subduction and crustal melting

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Keywords: U-Pb geochronology, zircon, monazite.

Metamorphism at high temperature and pressure can proceed at different rates, from several cm/year to fractions of mm/year. This talk will explore the relation between tectonic setting and rate of metamorphism during collisional orogenies. U-Th-bearing accessory minerals are ideal for determining rates and duration of high-grade metamorphism because they record and preserve overprinting stages of metamorphism, and their age can be linked to metamorphic conditions using textures, inclusions, thermometry and trace elements.

In-situ geochronology of zircon, titanite and allanite in high-pressure rocks of the Western Alps indicates short duration of metamorphic cycles. Relatively small slices of high-pressure rocks were exhumed fast, in the order of several cm/year. A double cycle of subduction-exhumation-subduction (yo-yo subduction) occurred in less than 20 million years and testifies to the dynamic nature of oblique convergence. The fast rate of subduction and exhumation recorded in the Alpine eclogitic units remains a challenge for tectonic models. These fast rates are in contrast with the slower rates determined for high-pressure metamorphism of larger crustal units, which thus followed a different tectonic evolution.

Multiple zircon, allanite and monazite domains can form during regional anatexis of crustal rocks. Geochronology of samples from migmatites in the Central Alps and Sikkim Himalaya indicates protracted high temperature regimes lasting over 10 million years. The preservation of melt layers and the variation in absolute ages within and between samples give insight into the dynamics of anatexis in these long-lived systems. Protracted anatexis and fast cooling require thermal models that maintain high temperatures and low melt production, and are coupled with fast tectonics. Short-lived anatexis is instead documented in the Chugach Metamorphic Complex, southern Alaska, where zircon and monazite crystallization occurred over a few million years on a ~200 km long section of the orogen. The fast Alaskan tectonic is the result of a different tectonic setting than the thick orogenic roots of the Alpine-Himalayan system.

### Garnet-bearing quartz diorites as clues for melting and melt extraction processes in the lower crust (Capo Vaticano Promontory, southern Italy)

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Keywords: crustal melting, peritectic garnet, Calabria.

The Serre Massif and Capo Vaticano Promontory (central Calabria) represent a segment of the Calabria-Peloritani Orogen that, in addition to representing a nearly complete section of late Paleozoic continental crust, preserve in its intermediate portion a relatively small batholith (Serre Batholith; Fiannacca et al., 2015 and references therein) with a wide range of granitoid rocks, that largely crop out together with their potential lower crustal source rocks. These particular features allow us to investigate on the mechanisms of production, differentiation and emplacement of granitic magmas. In particular, some singular quartz diorites, intruded in metapelitic migmatites forming the top of the lower crust section, stand out for their unusual garnet content (>20 % vol.) which appears in crystals with a diameter that frequently overcomes 30 mm (Clarke & Rottura, 1994). Garnet occurs in euhedral to subhedral crystals, surrounded by a leucocratic matrix mostly composed by 5 to 20 mm-sized euhedral plagioclase, minor biotite (0.5-1.5 mm in size) and rare interstitial quartz, arranged to form an adcumulitic-type structure. Garnet-bearing quartz diorites often contain cm- to dm-sized metapelitic enclaves, composed by plagioclase (30-35% vol), quartz (25-30% vol) and biotite (5-20% vol), and characterized by a fine-medium grain size (1-3 mm) and local anisotropic relict domains in a dominant decussate fabric. Garnet can be commonly found also inside the metapelitic rocks, usually surrounded by a plagioclase halo. Garnet crystals are characterized by core-to-rim inclusions of biotite, plagiocase and quartz with features similar to those of the same mineral phases in the metapelic enclaves, suggesting garnet nucleation and growth inside the metapelite. Garnet would therefore represent a peritectic phase produced by dehydration melting of the hosting metapelites after intrusion of the earliest granitoid magmas from the batholith. Garnet occurrence and preservation as dominant mafic phase, together with observed cumulitic texture, suggests an origin of these unusual quartz diorites as a dominantly solid residuum after escape of a hydrous granitic melt. Image assisted thermodynamic modelling supported by quantitative microstructural analysis of microdominial equilibria to estimate the effective reactant volume is in progress, with the main aim to get constraints on the possible processes of melting and melt extraction at specific PT conditions.

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# Fossil intermediate-depth earthquakes in subducting slab mantle linked to differential stress release

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Keywords: Pseudotachylyte, Intermediate depth earthquakes, subduction zone.

Intermediate-depth subduction-zone earthquakes (50-300 km) are inaccessible to direct investigation. Knowledge relies on seismic data, rock-deformation experiments and modelling, showing that the seismic activity concentrates either inside the subducting lithosphere, or in km-thick hydrated layers along the plate interface. In comparison, field-based studies of exhumed high-pressure rocks are underutilised to study fossilized earthquake phenomena. The cause of intermediate-depth seismicity in subduction settings is uncertain, but is typically attributed to rock embrittlement associated with fluid pressurization, or to thermal runaway instabilities.

We show the exceptional preservation of glass in pseudotachylyte that formed under eclogite-facies conditions (60-70 km depth; Scambelluri et al., 2017) in oceanic gabbro-peridotite from the Lanzo Massif (Western Alps), a fossil analogue to oceanic lithospheric mantle undergoing present-day subduction. The studied gabbro-peridotite is poorly hydrated to dry: the rocks show a high-temperature mantle-to-oceanic mylonitic foliation, but escaped crystal-plastic deformation (and largely metamorphism) during subduction and exhumation. The dry gabbro-peridotite section contains minor volumes (5vol%) of hydrated metaperidotite and metagabbro showing static, eclogite-facies metamorphism.

In dry, unaltered gabbros, pseudotachylytes preserve pristine glass including microlites of olivine, plagioclase, clinopyroxene and pyrope-rich garnet. Raman analysis establish that the glass is dry. Within peridotite pseudotachylyte did not preserve glass, but consists of a microcrystalline annealed groundmass and microlites. Pseudotachylytes cut through the eclogitized metagabbro and metaperidotite: delopment of cataclastic clinopyroxene cemented by omphacite and overgrowth of damage microfaults by eclogitic garnet indicate that pseudotachylytes developed at 550 °C, 2.1 GPa. These pseudotachylytes are therefore hosted in near anhydrous lithosphere free of coeval ductile deformation, which excludes an origin by dehydration embrittlement or thermal runaway processes. This indicates that seismicity can be explained by the release of differential stresses accumulated in strong, dry, metastable rocks.

Survival of glass and the absence of subduction-related ductile deformation demonstrate the control of aqueous fluids over the kinetics of metamorphic reactions and rheology. The development of mantle and oceanic high-temperature foliations (ca. 800 C) indicate a temperature threshold for crystal-plastic deformation to occur in these dry rocks, consistently with the temperature cut-off for both the oceanic environment and intermediate depth seismicity in subducting plates. These rocks represent a proxy for the rheological behaviour of a subducting dry oceanic lithosphere, which is rarely exposed in exhumed orogenic accretionary wedges that mainly incorporate material from the fluid-rich subduction channel.

Scambelluri, M., Pennacchioni, G., Gilio, M., Bestmann, M., Plümper, O., & Nestola, F. (2017): Fossil intermediate-depth earthquakes in subducting slabs linked to differential stress release. Nature Geoscience, 10(12), 960-966.

### Anticlockwise P-T metamorphic evolution of retrogressed amphibolites from NE Sardinia, Italy: geodynamic implications

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Keywords: amphibolite, garnet zoning, metamorphic evolution.

Within the Migmatite Complex from NE Sardinia, in the Golfo Aranci Area, an hectometric lensoid amphibolite body crops out. Inside this body two main lithologies can be distinguished: retrogressed amphibolites and ultramafic amphibolites. The retrogressed amphibolites are coarse-grained, dark-green rocks with a schistose to weakly massive aspect. These rocks have experienced a massive retrograde amphibolite-facies overprint, which made it difficult to find relics of early-stages metamorphic history. The main feature these rocks can show is the occurrence of centimetric-sized layers featured by large garnet porphyroblasts. These layers, oriented parallel to the regional schistosity, consist of millimetric (up to 1 cm) euhedral and subhedral garnet porphyroblasts in a matrix of green amphibole, plagioclase, quartz and aggregates with a clinopyroxene + plagioclase fine-grained symplectite-type texture. We investigated the layers inside the retrogressed amphibolites with microstructural analyses and thermodynamic modelling in order to reconstruct their P-T metamorphic evolution. Garnet porphyroblasts, which can reach 30% vol. in these layers are almandine rich (56-59 mol%) and spessartine poor (1-7 mol%), with intermediate grossular (26-28 mol%) and pyrope (10-16 mol%) contents.

P-T path has been reconstructed by P-T pseudosection modelling in the NCKFMASH+Ti+Mn system to garnet bearing layers. The studied amphibolites underwent an anti-clockwise P-T path, recorded by the different compositional zoning of garnet core and rim. The P-T path recorded got across the granulite- to the high-pressure granulite-facies with a pressure increase of 0.3-0.7 GPa and a slight increase in temperature. The garnet rim recorded the peak conditions at T=680-720 °C and P=1.3-1.4 GPa. The layout of the garnet isomodes confirmed that garnet porphyroblasts stopped their growth after reaching the peak pressure and, thus, before the decompression phase characterized by the growth of amphibole. The obtained anti-clockwise P-T path is in contrast with the clockwise P-T paths documented for several HP metamorphic rocks from NE Sardinia.

We interpreted this anti-clockwise path as if the studied rocks were located in the lowermost part of the upper plate during the continental collision between Laurussia and Gondwana during Variscan orogeny. At that time, the amphibolites were brought to depths of around 45 Km and subsequently were exhumed by a back-thrusting event that involved continental slices from both upper and lower plate (the HP metamorphic rocks from NE Sardinia) and remnants of the subducting oceanic crust (the eclogites from NE Sardinia) in an exhumation channel.

### High-temperature overprint in high-pressure rocks from Monte Duria (Adula Nappe, Italy): clues for the subduction/exhumation history of the Central Alps

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Keywords: Adula-Cima Lunga unit, Central Alps, high-temperature overprint.

The Adula-Cima Lunga unit (Central Alps) belongs to the lower Penninic domain, which is considered to derive from the former European continental margin. It consists of orthogneiss and paragneiss of pre-Mesozoic origin hosting lenses of metacarbonates, partly retrogressed eclogites and garnet/chlorite peridotites. During the Alpine orogenesis, in late Cenozoic, rocks now part of the Adula Nappe were subducted to mantle depths. The peak conditions of the HP metamorphism increase from north to south from 1.7 GPa and 650 °C up to 3 GPa and 800 °C, even if an older HP event of Variscan age is preserved within eclogite boudins of the central and northern portion of the Adula Nappe. After the European margin subduction beneath Adria, the HP rocks of the Adula Nappe were overprinted by an amphibolite-facies metamorphism, postdating the main phase of nappe-stacking.

The highest P-T conditions were recorded by garnet lherzolites cropping out at three localities: Cima di Gagnone (CdG), Alpe Arami (AA), and Monte Duria (MD). These peridotites show transitions to eclogite and occur as lenses surrounded by meta-ophicalcite rocks (CdG), marbles, kyanite eclogites (AA) and migmatitic gneisses (MD). In this work we present a petrological study of peridotites and different types of eclogites occurring in the MD area, which share a common eclogite-facies peak at P=2.6-3.0 GPa and T=710-750 °C. Differently from CdG and AA, the HP minerals of MD peridotites and eclogites are replaced by lower-P and high-T assemblages. In peridotites, the zirconium titanate srilankite occurs as µm-sized crystals in textural equilibrium with spinel, clinopyroxene and orthopyroxene in kelyphites developed between garnet and olivine. By using a new ZrO<sub>2</sub>-TiO<sub>2</sub> solid-solution model, we demonstrated that srilankite is stable in peridotites at T>810 °C at  $P\approx 0.9$  GPa, consistent with estimates of  $T\approx 850$  °C retrieved from symplectites in garnet fractures consisting of sapphirine+spinel+Al-orthopyroxene+amphibole. In eclogites, kyanite is replaced by symplectites made of anorthite-rich plagioclase+spinel±sapphirine±corundum, formed at  $T\approx 850$  °C and P=0.8-1.0 GPa, coincident with the high-T overprint recorded by the peridotites. Contrary to the consistency between these estimates for the HP peak in MD and previous ones on garnet peridotites and some eclogites of the Adula-Cima Lunga Nappe, the observed HT granulite-facies overprint postdating the eclogite-facies stage was never reported so far in the Central Alps. This evolution from eclogite- to granulite-facies conditions is known from the orogenic evolution of the Variscan cycle. Particularly, HT conditions are attributed to the Permian-Triassic igneous activity resulting from rifting activity that followed the collapse of the Variscan belt. Our new data add one more piece to the puzzle of the Central Alps, where the interplay of Variscan and Alpine geodynamics conceals the tectonometamorphic evolution and age of metamorphism of each unit.

### New insights for the tectono-metamorphic evolution of the upper-intermediate crustal section exposed in the southern Serre Massif (Calabria, Southern Italy): phase equilibria modelling of a garnet-hornblende bearing metandesitic lense

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Keywords: Variscan orogeny, garnet-hornblende metandesites, P-T path.

The reconstruction of the tectono-metamorphic evolution of the Variscan intermediate and upper crustal section exposed in the southern Serre Massif (Calabria, southern Italy) is crucial for a broader understanding of the crustal dynamics during the Variscan orogeny. In the southern Serre Massif, Variscan tectonics juxtaposed the Mammola Paragneissic unit (hereafter MPu), representative of the intermediate crust, and the Stilo-Pazzano Phyllite unit (SPu), representative of the upper crust. Subsequently, both units were affected by a contact metamorphic event related to the emplacement of the Upper-Carboniferous Serre batholith. Within the MPu, in the Levadio Stream area, garnet-hornblende bearing metandesitic lenses are locally interlayered with the paragneisses. The juxtaposition of the MPu and SPu is marked by a mylonitic shear zone affecting also the metandesite.

This study examines via phase equilibria modelling the metamorphic evolution of a sheared garnethornblende bearing metandesite. To this purpose, the rock was modelled in the MnO-Na<sub>2</sub>O-CaO-K2O-FeO-MgO-Al<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O-TiO<sub>2</sub>-O system using the software THERMOCALC v.3.45, with the thermodynamic dataset ds63, including a - x models for both metapelitic and metabasic minerals. The pre-peak metamorphic mineral assemblage (ep-q-pl-mu-chl-bi-rieb) is hosted as primary inclusions in garnets having the following composition: almandine (50-53%) - grossular (29-31%) - spessartine (17-20%). The constructed P-T pseudosection shows that the peak mineral assemblage (g-ep-mu-bi-chl-rieb-ab-sph-q-H<sub>2</sub>O) was stable in a wide, low-variance P-T field of 6 - 13 kbar and 350 - 525 °C. Garnet isopleth modelling suggests P-T conditions for the regional metamorphic peak of 7.9 - 9.2 kbar and 495 - 510 °C. The subsequent, near isothermal exhumation from about 32 to 10 km depth at 450 - 500 °C brought the metandesite close to the emplacement level of the Serre batolith (at 2.7 kbar). The constructed T-M<sub>H20</sub> pseudosection points to T values of 570 - 593 °C for the peak pl-bi-q-g-hb-sph mineral assemblage of the contact metamorphism, under H<sub>2</sub>Osaturated conditions. The derived P-T path for the garnet-hornblende bearing metandesite is consistent with the one derived by Angi et al. (2010) for the MPu paragneiss, and highlights that comparable peak pressures were reached at the regional metamorphic acme in the southern Serre Massif within the MPu, as well as within the granulite facies rocks cropping out in the north. This suggests that the thermal gradient significantly changed across the Variscan chain exposed in Calabria in response to distinct tectono-magmatic contexts.

Angì, G., Cirrincione, R., Fazio, E., Fiannacca, P., Ortolano, G. & Pezzino, A. (2010): Metamorphic evolution of preserved Hercynian crustal section in the Serre Massif (Calabria-Peloritani Orogen, Southern Italy). Lithos, 115, 237-262.

#### Applying elastic geobarometry on the Lago di Cignana UHPM unit: preliminary results

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Keywords: geobarometry, metamorphism, subduction.

Elastic geobarometry of host-inclusion systems is increasingly recognized as an alternative to conventional geobarometry as it overcomes several issues with applying the latter. Whereas conventional geobarometry relies on equilibrium between specific mineral pairs, elastic geobarometry regards the elastic behaviour of inclusions and their host mineral. Common metamorphic minerals such as quartz and zircon included in garnet can be used, allowing this technique to be applied in a wide range of settings. The processes that form issues for conventional geobarometry, for example diffusion or chemical disequilibrium, have less impact on elastic geobarometry.

Elastic geobarometry is based on the development of residual stresses inside inclusions of common metamorphic minerals in a rigid host (e.g. garnet) during exhumation as a result of a difference in elastic properties. The pressure during entrapment can be calculated based on these residual stresses. Several common processes in metamorphic rocks may affect the suitability of garnet as a host. Mineral dissolution can release stresses inside inclusions if the garnet is dissolved down to near the inclusion. Furthermore, plastic deformation of the garnet host can complicate calculations of entrapment conditions based on strain measurements, as the initial assumption is made that all deformation in elastic host-inclusion systems is elastic.

Using elastic geobarometry, the metamorphic evolution of the Lago di Cignana ultra-high pressure metamorphic rocks will be reassessed. Chemical, mineralogical and microstructural analyses are performed on the garnets from a quartzite of the Lago di Cignana unit in order to determine their quality as host for elastic geobarometry. Although the majority of the rock matrix represents retrograde processes, the garnets have recorded and preserved a complex history of growth and dissolution phases during subduction metamorphism. Further results on the potential and application of elastic geobarometry of these garnets will be discussed here, as well as their implications.

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### Permian geodynamics of the central Southalpine by tectono-thermal record in post-Variscan conglomerates

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Keywords: Microstructural and petrologic analysis, Pangea break-up, geodynamic modelling.

The central Southern Alps consist of the pre-Alpine basement and Permian-Mesozoic covers, both affected by the Alpine fold-and-thrust belt. The pre-Alpine basement recorded heterogeneous structural and metamorphic evolutions and therefore consists of different tectono-metamorphic units related to different stages of the Variscan evolution. To the east, rocks recorded the effects of the Variscan tectonic burial and escaped the subsequent collision, whereas the units outcropping westward recorded both the effects of Variscan tectonic burial and collision and the westernmost basement rocks even host late-Variscan intrusives and recorded the effects of lithosphere thinning-related Triassic high-temperature (Spalla et al., 2014). Lower Permian volcanoclastic sequences infill intermontane basins and are the oldest sedimentary rocks uncoformably capping the basement (Berra et al., 2016; Zanoni & Spalla, 2018 and refs therein). These sequences consist of volcanites overlaid by lacustrine sandstone and alluvial fan conglomerates. According to radiometric constraints, the age of the conglomerates is more recent westward. These conglomerates contain pebble- to boulder-sized crystalline clasts. The metamorphic evolution recorded in clasts are related to the Variscan orogeny and revealed that the thermal maturity of orogenic traces increases westward, likewise the general record in the metamorphic basement, indicating that conglomerates were fed by the erosion of tectono-metamorphic units similar to those exposed today. In the westernmost conglomerate, clasts recorded high-temperature metamorphism and some derive even from late-Variscan intrusives and later tourmalinite-breccia. Since the conglomerates rejuvenate westward with the increase of orogenic maturity in clasts, we speculate that the post-Variscan lithosphere was affected by westward propagating extension, also responsible for intermontane wrenching. To test this hypothesis, we started 2D numerical simulations on the thermo-mechanical evolution of the lithosphere affected by westward propagating extension.

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- Spalla, M.I., Zanoni, D., Marotta, A.M., Rebay, G., Roda, M., Zucali, M. & Gosso, G. (2014): The transition from Variscan collision to continental break-up in the Alps: insights from the comparison between natural data and numerical model predictions. Geol. Soc. London Spec. Publ., 405, 363-400.

Zanoni, D. & Spalla, M.I. (2018): The Variscan evolution in the basement cobbles of the Permian Ponteranica Formation by microstructural and petrologic analysis. Ital. J. Geosci., 137, <u>https://doi.org/10.3301/IJG.2018.12</u>.

# Session S12

# Georesources and Energy for the XXI Century

Conveners AND CHAIRPERSONS Fabrizio Agosta (Università della Basilicata) Roberto Gambini (ENEL) Sergio G. Longhitano (Università della Basilicata) Stefano Mazzoli (Università di Napoli Federico II) Giorgio Minelli (Università di Perugia) Emanuele Tondi (Università di Camerino) Pierluigi Vecchia (Strata GeoResearch srl) Emilio Tebaldi (ENI)

# Numerical simulations of the industrial process of storage of natural gas in order to investigate the safety of a real depleted tank

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Keywords: natural gas storage and production, geological reservoir, 3D numerical modeling.

The storage of natural gas in underground structures known as geological deposits plays a key role in the Italian energy system. Gas storage is an industrial process designed to meet requirements such as responding to market gas demands, managing production facilities and transportation networks and ensuring the maintenance of strategic reserves to be used exclusively to cope with exceptional situations.

The studies on the conservation of natural gas are particularly interesting also for analyzes related to seismicity. In fact, recent seismic events have emphasized the attention on the safety aspects related to this industrial process.

In geological basins where gas storage takes place, factors such as fluid dynamics, processes and the response of geological formations are strongly interconnected. In this context, numerical modeling plays a very important role as it is the only tool that allows scenario analysis to be carried out.

This activity concerns the study, through numerical simulations, of the industrial process of storage and supply of gas in a reservoir. In addition, an increase in storage capacity was also considered with the exercise of overpressure fields compared to the base reservoir at the time of the discovery of the reservoir. These additional gas capacities would have a positive impact on the energy system, in terms of ensuring the supply of raw materials and increasing flexibility.

For demonstration purposes, the characterization of a natural gas storage site has been done, located in Lombardy, called "*Sergnano virtuale*" in which several wells with storage and supply functions are active. The site was chosen according to the availability of data: in fact, for the fields in operation, the necessary information represents sensitive data and therefore not public. The collection of information on the geological formations, the creation of the 3D static geological model and the corresponding 3D fluid dynamic model were carried out. The simulation process was rather accurate and able to correctly replicate the tank conditions over time, both in terms of gas volume and the distribution of operating pressures along the wells and the position of gas water contact (GWC).

Subsequently, a simplified modeling approach was applied to simulate geo-mechanical interactions using a dedicated code. The analyzes were performed considering a stationary regime with some simplifications such as: mono-directional modeling coupling without influence of the geo-mechanical phase on the fluid one, constant temperature, absence of discontinuity in the fields of effective tensions. Using the fluid dynamic results obtained for the "*Sergnano virtuale* " reservoir, the field of displacement vectors was calculated in order to verify the stress generated in the reservoir rock. From the results of the geo-mechanical interactions it is possible to notice the deformation of the various formations that spreads up to the ground level.

### Using Rock Fracture Knowledgebase for environment and energy and related issues

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Keywords: Rock Fracture Knowledgebase (RFK), Web Ontology Language file (WOL).

The Rock Fracture Knowledgebase (RFK from here on) is a repository of information about rock fracturing and the resulting structures. It is an Internet-based tool and can be utilized as a resources for energy and environmental issues. In this presentation, we first introduce the RFK and then highlight webpages related to energy and environment.

The content of RFK is stored in a Web Ontology Language (OWL) file. The OWL file is translated and formatted to individual web pages by Extensible Stylesheet Language Transformations (XSLT) and finally is edited by Protégé, an ontology editor.

The RFK contains four major classes of structures: Joints, Faults, Pressure Solution Seams, and Deformation Bands. The classes are organized based on hierarchical tree structure, starting from the Home page and branching off to more specific ones linked by hyperlinks. For example, 'Home page' -> 'Fractures' -> 'Faults' -> 'Shear Bands' -> etc... There are also hyperlinks that connect related structure classes. For example, the class 'Shear Bands' has hyperlinks to 'Mechanisms and Mechanics of Shear Bands' and 'Petrophysical Properties of Shear Bands'. Readers can chose the path of navigation, traverse the tree, follow the related links, or jump directly to other concepts of interest from a highly extensive list in the 'Table of Contents'.

The RFK is completely digital and is accessible on the Internet by computers, tablets, and smart phones by multiple users at the same time from anywhere provided Internet access. Comparing to traditional printed books with chapters, the Knowledgebase consists of individual web pages covering the concepts with virtually unlimited text, illustrations, and references. The overriding message is that knowledge is too valuable to waste and the RFK is a contribution to this goal in geosciences.

### 3D Structural Modeling and Restoration in thrust belts: examples from the Kumeta and Busambra Mts, Sicilian fold and thrust belt, Italy

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Keywords: 3D structural model, 3D restoration, Sicilian Fold-and-Thrust belt.

3D structural modelling allows to represent the geometry of surface and subsurface structures to produce reliable forecast, in structurally complex geological settings. In addition to modelling, restoration is one of the existing techniques applied to validate structural interpretations of geological units, defining whether the model is geometrically consistent or not. Restoration is generally used to reduce the exploration risks when seismic imaging is of poor quality or inexistent. 2D restoration is a popular technique used in structural geology but it does not consider out-of-plane movements. On the contrary, 3D restoration allows lateral movements in any direction, representing a recommended technique for not-coaxial fold and thrust belts.

The Sicilian Fold and Thrust belt represents a complex area characterized by shortening variations, different exhumation rates, and various syn-tectonic sedimentation and structural style along strike. Reconstruction of 3D geometry of geological structures in such areas represents a real challenge as 2D onshore seismic lines are unclear or incomplete and this uncertainty makes several scenarios possible. To validate the most reliable interpretation, 3D restoration represents a fundamental tool.

Our study area is located in Western Sicily (Kumeta and Busambra Mts) and extends for about 870 km<sup>2</sup> Seismic lines, logs interpretation and field data allowed to reconstruct the 3D structural model. The interpreted horizons are: top of Cretaceous limestones and top of Miocene marls for the lowermost unit; top of Cretaceous limestones and top of the late Oligocene-lower Miocene flysch for the uppermost unit. Major faults with more of 500m of displacement were represented. A variation of structural style along strike is recognized: from south verging structures in the western part of the area to north verging structures in the eastern part. From the 3D structural models two kinematic evolutionary scenarios can be envisaged: either a single step or a two-step thrust-fault deformation. The 3D model reconstruction coupled with 3D geomechanical restoration of the lowermost unit in the two geometric-kinematic scenarios was performed in order to validate which of them represents the best solution.

#### **3D** Nanopores tomography using transmission electron microscopy in Triassic Dolostones

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#### Keywords: Porosity, Reservoir quality, Tomography.

Triassic dolostones of the northern Calabria have proven to be influenced by complex diagenetic and depositional processes that led to the formation and preservation of micro- and especially nano-scale porous networks (Perri et al., 2017). As the characterization of nanopores has become a major challenge in the reservoir modeling field (Słowakiewicz et al., 2016), we propose a new technical approach, using transmission electron microscopy (TEM) tomography, to tridimensionally characterize the nano-scale pores network. Firstly the pore system was studied by mercury porosimetry (MICP) in the dimensional range of 360  $\mu$ m to 3 nm and by low pressure N<sub>2</sub> adsorption analysis in the range of 150 nm to 0.3 nm. MICP revealed low porosity (2.3%) and low permeability (0.11 mD) while, pores mainly consist of nanopores (94%) and less micropores (6%). Nanopores show a prevalent diameter of ~50 nm and minor dimensional classes of pores with diameters of 25, 12, 6, 2 nm. As the hysteresis loop of N<sub>2</sub> adsorption/desorption curves nano pores are characterized by slit- or wedge-morphology.

SEM imaging analysis revealed that nanopores are mostly intercrystalline and subordinately intracrystalline. The intercrystalline pores consist of the spaces between the crystal faces forming an apparently well connected network; whereas, the intracrystalline pores consist of apparently isolated pores with mostly polygonal section.

As TEM presents a higher-magnification capacity than SEM, allows, working with transmitted electrons, to reconstruct an accurate 3D model of nanopores, through an application for tomographic sectioning and morphological reconstruction. The 3D model of the intracrystalline pores confirms their sub-polyhedral shape, but shows that these pores can be opened elongated "channels" up to hundreds of nm crossing the entire dolomite crystals, and thus potentially interconnected. However, although limited, the presence of blind intracrystal nanopores, consisting of few tens of nm polyhedrons, has been confirmed by TEM tomography. The presence of intracrystalline-closed pores with possible fluid- or gas-inclusion is also supposed. Furthermore, tomography reconstructions show a further nanopore type, consisting of opened slit, most probably nano-fractures, crosscutting crystal faces.

In conclusion, the 3D reconstruction of nanopores by TEM tomography can significantly integrate the more traditional techniques, as it is an efficient new methodology to better characterize the nano-scale pore system of rocks and to perform more accurate reservoir quality prediction.

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Perri, E., Borrelli, M., Spadafora, A. & Critelli, S. (2017): The role of microbialitic facies in the micro- and nano-pore system of dolomitized carbonate platforms (Upper Triassic e Southern Italy). Mar. Petr. Geol., 88, 1-17.

### Outcrop-scale fracture analysis of tight, well-bedded, Lower Cretaceous limestones, Monte Alpi (southern Italy)

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Keywords: Fractured carbonate, Discrete Fracture Network, modelling.

On a global scale, ca. 50% of natural oil and gas reserves are hosted in carbonate rocks. Commonly, both fluid storage and flow properties of these rocks are often dependent upon nature, geometry intensity and connectivity of the fracture network that crosscut them. In order to evaluate the hydraulic properties of tight carbonate matrices crosscut by either a diffuse or a localize deformation, this study focuses on the limestones exposed at the Monte Alpi, southern Italy, which pertain to the Inner Apulian Platform. By combining field and laboratory analyses, we present the results of outcrop-scale structural analysis, micro-scale petrographic analysis of representative limestone samples, and DFN modeling. The goal is to compute the amount of both fracture porosity and equivalent permeability of outcrop-scale, geocellular volumes crosscut by Strata Bound fractures (SB), which represent the limestones cropping out away from major fault zones, and also by Non Strata Bound fractures (NSB) as documented in the study fault damage zone. The study limestones are characterized by a wide spectrum of calcareous facies, from mudstones to grainstones, which were deposited in moderate water energy environment. Results of field structural analysis are consistent with SB fractures being characterized by a Poissonian distribution, forming not clustered configurations within the individual limestone beds. There, bed interfaces are hence interpreted as mechanical interfaces that inhibited the vertical propagation of mode I fractures, joints, which form two cross-orthogonal, bed-perpendicular sets that developed, more or less, at the same time due to a stress-state transition mechanism. Within the fault damage zones, NSB fractures offset up to a few cm the individual bed interfaces, forming a conjugate system sub-parallel to the main slip surfaces. Results of Discrete Fracture Network modelling of geocellular volumes representative of the surveyed outcrops show that the fault damage zone form the main repository for underground fluids, in which NSB fractures act as main control on fracture porosity, and determine almost isotropic horizontal fluid flow properties. This study highlights therefore the importance of studying surface structural analogues, which may provide useful information for the management and development of subsurface fractured carbonate reservoirs.

# The Monte Vulture Volcano (Southern Apennines; Italy): evidences of past hydrothermal circulation and inferences on geothermal potential

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Keywords: Monte Vulture Volcano, Southern Apennines, hydrothermal system.

In the Apennines, hydrothermal systems are quite common in the extensional areas of the inner sector of the chain. In this work, we analyse a fossil hydrothermal system located along the eastern flanks of the Middle Pleistocene Vulture Volcano, which lies along the outermost edge of the belt. The study site hence provides an unique opportunity to investigate the interplay between shallow-rooted faulting associated to thrusting and hydrothermal fluid circulation.

The site is exposed along the eastern flank of the Vulture Volcano, where the entire footwall damage zone of a trastensional, high-angle fault is exposed along the walls and pavements of an inactive quarry. The damage zone is mineralized by both jarosite and amorphous silica veins. The latter phase is also present within the rock matrices. Moreover, the damage zone is characterized by the presence of Fe-oxyhydroxides along the main slip surfaces.

By integrating the results of both meso-and micro-structural analysis with detailed X-Ray diffraction (XRD) and fluid inclusion (FI) studies, we provide new data to better constrain the time-dependant evolution of this fault-controlled hydrothermal system. The results of XRD analysis are consistent with three main phases of mineralization. The first is characterized by jarosite, suggesting low pH (~3-4) conditions, temperature < 200°-250°C and a high activity of the SO<sub>4</sub><sup>2-</sup>, which is typical of advanced argillitic alteration facies. The second phase consists of amorphous silica-rich veins, which reflect lower temperature conditions (T< 100-120°C). The third, and younger, phase is dominated by goethite that suggests higher pH values with respect to the first phase, and low T conditions (T< 100°C). FI investigation was performed in order to provide constraints on T conditions of fluids circulated in the area. Secondary FI trails were observed within quartz crystals flanking the jarosite veins. These are generally two-phases liquid-rich FI; rare monophase FI (liquid) were also documented. Microstructural observations show that secondary FI are present within microfractures that are sub-parallel to the main slip surfaces. The studied two-phase FI exhibit a relatively wide temperature of homogenization range between 165° and 263°C, with a mode at 200°C.

All the data hence confirm that deep, hot, fluids, which were likely enriched in  $SO_4^{2-}$  during their ascendance from depth along the high-angle faults crosscutting the Apulian Platform, were able to circulate within the footwall damage zone. Precipitation of jarosite within the vein sets is interpreted as the main product of this hydrothermal circulation. Subsequently, amorophous silica precipitated from lower T fluids in both open fractures and rock matrices due to dismantling of the feeding system associated with the abrupt arrest of contractional deformation. Later precipitation of goethite along the main slip surfaces was probably due to weathering.

### Geological and numerical fluid dynamic modelling of Sulcis basin in Sardinia for CO<sub>2</sub> geological storage

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Keywords: CO, geological storage, 3D modelling, Fluid dynamic.

The study shows the results of a geological and numerical modelling of the "Monte Ulmus" exploration permit located in Sulcis basin (South-Western Sardinia - Italy) for testing a pilot project on  $CO_2$  geological storage. An accurate 3D geological model has been realized thanks to the researches developed during the exploitation of the existing coal mine and by processing a set of wells and seismic reflection lines realized inside the exploration permit. The potential reservoir for  $CO_2$  storage is represented by the Miliolitico geological formation with Eocene age and consisting of a bio-calcarenite with a thickness around 50-70 m. The Cixerri formation (Miocene-Oligocene age) plays the role of caprock to avoid  $CO_2$  leaks thanks to the remarkable presence of clay deposit and a thickness generally greater than 300 m.

The fluid dynamic model has been implemented considering the petrophysical proprieties of the referring geological formations and the geothermal gradient with a focus on a 30 km<sup>2</sup> sector of the western basin. The 3D generated mesh consists of 41 vertical layers with a thickness variable between 5 and 220 m for a total of about 124,000 elements and 116,000 interconnected nodes; the vertical extension of the mesh is between 100 m asl and -2,200 m of depth.

Three structures of injection wells have been elaborated considering areas with different thickness of the caprock and different  $CO_2$  injection depths and respectively equal to 850, 1,350 and 1,100 m. The imposed  $CO_2$  volume for injection was of 100,000 tons and nine numerical scenarios have been realized with different  $CO_2$  injection timing modes and different values of petrophysical parameters of the caprock. Two injection modes have been developed considering a constant  $CO_2$  flow and different period of one year and two years respectively. A third mode consisted of a step-injection of 25,000 ton/year during a period of four years with 6 months of  $CO_2$  injection followed by six months of break-timing.

The same scenarios have been reprocessed for a total of 21 tests considering different values of permeability for the caprock-reservoir system and x, y, z permeability heterogeneity. For all the scenarios the numerical simulation has been extended up to ten years to study the CO<sub>2</sub> plume extension changes after the end of CO<sub>2</sub> injection.

The obtained numerical results show how the injection modes and permeability parameter affect the  $CO_2$  plume extension and over pressure values inside the reservoir. The plume extension reaches the maximum of 520x400x330 m at the end of  $CO_2$  injection for a scenario with one year of  $CO_2$  injection and under favorable permeability condition. The maximum over pressure value of about 14 bar was estimated for another scenario with lower permeability condition but generally the values are lower and considering the scenarios with permeability heterogeneity the over pressure is lower 2 bar.

### Integrated petrophysical characterization in a complex brownfield

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Keywords: Petrophysical Characterization, Rock Type, k- Nearest Neighbour.

The integrated petrophysical characterization, aimed at subdividing the reservoir into homogeneous intervals from a lithological and petrophysical standpoint, can be very challenging in case of complex brownfields when available data are extremely wide and heterogeneous. This study shows the application of an innovative workflow for Reservoir Rock Type (RRT) definition, aimed at identifying facies with similar petrophysical properties (porosity and permeability) at the core scale that can be also valid at the log scale.

The reservoir is characterized by a typical continental sequence passing from alluvial deposits to fluvial, lacustrine and locally coastal sediments.

The integrated reservoir characterization started with a homogenization of the petrophysical interpretation (CPI) that was carried out integrating cores, logs, pressure data and information collected during years of production history. This step was mainly aimed at obtaining a more precise description of the rock matrix. A multi-mineral approach has been chosen and Quartz, Orthoclase, Calcite, Hornblende and Illite, were the selected minerals. This new model allowed to separate and characterize high density rocks corresponding to conglomerates with igneous and metamorphic clasts present in the upper part of the sequence that have been disregarded in the past.

RRT definition was based on Mercury Injection Capillary Pressure (MICP) data. This test consists of injecting mercury at increasing pressure steps in a core-sample, while measuring the incremental volume entering the pore system at each step. The result represents the distribution of the connected pore volume accessible by throats of a given size.

MICP data from 53 samples of 6 wells were used to identify 7 distinct RRT characterized by well-defined porosity and permeability ranges. The classification was obtained by clustering data of pore throats size distribution (from pores-throat less than 0.3  $\mu$ m up to larger than 10  $\mu$ m) and an efficiency index indicating the ratio between effective (>1 $\mu$ m) and non-effective throats in each sample. Furthermore, the k-Nearest Neighbour (kNN) technique has been used to extend the classification to all the existing plugs (>800) with only porosity and permeability from routine data analysis (RCA).

Finally the core rock types were successfully propagated into the log domain by clustering the responses of Total GR, Density, Neutron, Neutron-Density Separation, Photoelectric Factor (PEF) and Sonic logs. In this way a continuous RRT profile along the wells profile has been obtained. Each log facies is linked to the petrophysical properties from the CPI and has been cross-checked with the sedimentological facies.

The application of this innovative workflow resulted in a rock types classification linking petrophysical properties to geological attributes, easily reproduced by logs that provides a more robust driver for the construction of the 3D model and the estimation of the hydrocarbons in place.

#### A conceptual model for the Tuscan crustal magmatism: insights on geothermal systems

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Keywords: granite, geothermal system, intrusions.

The Tuscan crust, from Elba Island to Larderello, experienced a common tectono-magmatic evolution since Late Miocene. Post-orogenic extensional tectonics triggered thinning/heating of continental crust, production of peraluminous, boron-rich granite magmas in the lower crust, their subsequent emplacement at shallow crustal levels (granite plutons and laccoliths) and activation of hydrothermal systems involving magmatic, metamorphic and meteoric fluids. Only minor volumes of mantle-derived magmas (calcalkaline, shoshonitic and lamproitic) reached such shallow crustal levels. Magmatism progressively migrated from west (e.g. west Elba Island, 8.5-6 Ma) to east (e.g. Larderello, 4.3 Ma-Present) following the eastward propagation of the Apennine compressional fronts and the progressive rollback of the subducting Adriatic plate. As magmatism shifted to the east, older intrusions were progressively exhumed by tectonics and erosion. For this reason, granites are widely exposed at Elba Island, just cropping out along the Tuscan coast and still buried at 1500-4500 m in the Larderello area. The western intrusive complexes represent proxies for the active system triggering the Larderello geothermal field.

A still not fully deciphered balance between magma driving-pressure at depth, physical-chemical characters of melts and occurrence of structural traps in the shallow crust, resulted in the systematic emplacement of granite magma at plutonic/subvolcanic levels (3-6 km) with rare volcanic extrusions at surface. Magma focusing at such shallow depth is the key mechanism for establishing transient, high temperature conditions in the upper crust and for generating extremely high geothermal gradients like those currently measured at Larderello. The emplacement of flat granite plutons and laccoliths induced a complex spatial-temporal perturbation of both temperature and stress fields. According to their temperature (ca. 850°C) and volume (30-150 km<sup>3</sup>), granite intrusions were able to trigger transient ductile conditions during the prograde development of contact metamorphic aureoles. Inflation of intrusions resulted in: i) uplift of the overburden; ii) formation of localized sub-horizontal brittle-ductile shear zones; iii) gravitational displacement along low-angle extensional faults.

The net result was the formation of granite plutons mantled by contact metamorphic aureoles hosting intrafoliar subvertical fractures/tension gashes that acted as an efficient sink for high temperature fluids issued by either the granite magma or the metamorphic rocks. Geochemical and isotopic data on western analogues indicate that such high temperature magmatic-metamorphic hydrothermal systems did not interact with superficial meteoric circuits. Locally, the interference between damaged contact aureoles and regional structures (extensional faults, transfer zones) allowed magmatic/metamorphic fluids to migrate outside the aureoles, in distal areas, producing metasomatic skarn bodies.

#### Petrophysical and rock physical properties of carbonate fault rocks

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Keywords: fault, fault core micromechanics, carbonate fault rock.

The great potential of fault zones for geothermal or hydrocarbon energy or CO<sub>2</sub> storage is missed due to limited data on seismic and petrophysical properties fault zone rocks. Paucity of published data coupled with poor understanding of the effects of diagenetic processes (cementation, physical and chemical compaction) on the resulting porosity, impedes comprehension of the controls exerted by grain fracturing and rolling on pore type, geometry and connectivity in carbonate fault rocks. We investigate this topic using outcropping, extensional fault zones crosscutting the Lazio-Abruzzi and Campania-Lucania platform carbonates of central and southern Italy, respectively. The studies fault zones were exhumed from depths < 1.5 km during the Plio-Quaternary downfaulting of the Apennines fold-and-thrust belt. The exposed fault cores consist of grain- and matrix-supported fault rocks, which are partially cemented along the main slip surfaces. Fluidized layers of ultracataclasites with injection veins are present along the largest fault zones. We focus three basin types: calciterich Fucino and Agri Valley basins, dolomite-rich Mercure Basin and Vietri di Potenza area, and mixed calcite/ dolomite-rich fault rocks from the Sulmona Basin. We quantify the fault rock properties of: 1) composition and texture; 2) effective porosity and permeability; 3) geometry, type, and distribution of connected pores.

Our optical microscopy, digital image, XRD, and SEM-Cathodoluminescence analyses show similar cataclastic micro-mechanisms but different diagenetic evolutions in all fault rocks. For example, chemical compaction and multiple generation of cements dominate in the calcite- and the mixed calcite/dolomite-rich fault rocks; dolomite-rich fault rocks show predominantly physical compaction. Petrophysical data reflect these differences: (a) Porosity and permeability values are higher in the grain-supported, calcite- and mixed calcite/dolomite-rich fault rocks, and in the matrix-supported, dolomite-rich fault rocks; (b) Ultrasonic P-wave velocities at ambient laboratory conditions are higher in the cemented, calcite- and mixed calcite/dolomite-rich fault rocks, than in the grain-supported, dolomite-rich fault rocks, the grain-supported, dolomite-rich fault rocks, and stiff, sub-spherical pores in the cemented fault rocks. Vp-porosity relations show that the former fault rocks, whereas the cemented fault rock are characterized by molds due to a selective dissolution. On the other hand, all dolomite-rich fault rocks contain microfractures and were not affected by dissolution.

# New conceptual model for the Tocomar Geothermal System (Central Puna, NW Argentina): insights from geological, structural and geochemical data

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Keywords: fault-related, Central Andes, geothermal energy.

The outlining of conceptual models, even in the earliest stages, represents a paramount aspect for geothermal exploration since these schemes are by far the most effective cost-benefit tool. While analogue models of geothermal fields provide an overall picture of reservoirs, they do not help planning exploration programs as each area of geothermal interest is a function of site-specific variables. Thus, reconstructing stratigraphic and structural framework is fundamental for i) understanding the relationship among cap rocks, reservoirs and fluid circulation, ii) geothermal potential, and iii) planning resource exploitation. Limited geothermal resource assessment in Argentina is based on weak exploration approaches as anomaly hunting or anomaly stacking, more than on realistic conceptual models generated from detailed geological information. In this sense, a new conceptual model for the Tocomar Geothermal System (TGS) based on geological, structural and geochemical data along with the available geophysical data is presented. The TGS is located in the Central Puna (Central Andes, NW Argentina), related to the 0.57 Ma Tocomar volcanic center (TVC) emplaced in a small extensional basin "Tocomar basin (TB)" linked to the active NW-SE trans-Andean tectonic lineament known as Calama-Olacapato-Toro (COT) fault system. The pre-basin succession is made of low-grade metamorphic and sedimentary lower Paleozoic rocks, Cretaceous continental rift-related deposits and ignimbrites from the Aguas Calientes Caldera (10-17 Ma). The basin infill consists of a thick alluvial deposit formed by polymictic conglomerates and sandstones that evolve upwards to several pyroclastic deposits.

The updated conceptual model for the TGS consists of a heat source related to the 0.57 Ma rhyolitic magmatic activity of the TVC. The geothermal reservoir has a NW-SE geometry elongated along the COT-like Chorrillos fault, with a minimum area of ca. 6 km<sup>2</sup>. The average depth of the top of the reservoir is 1,000-1,400 mbgs, probably hosted in Cretaceous sedimentary rocks. The primary permeability is enhanced by intense deformation along the COT. Both the interbedded fine-grained Cretaceous facies and a hydrothermal clay cap (argillic alteration) act as seal rocks. Hot springs occur in association with deep N30-N60 fractures related to the COT. They show a Na-Cl composition, with pH values of 5.84 to 6.87, and outlet temperatures ranging from 30.3°C to 70.2°C. Temperature estimation using the NA-K geothermometer indicates reservoir temperatures of 184-230°C. Estimated local geothermal gradient for the TB is ~150 °C/km and the minimum stored heat in the geothermal reservoir is of about  $3.21 \times 10^{15}$  kJ.

# The role of geology in the optimization of low-enthalpy geothermal systems: a case study from the Island of Salina (Aeolian Islands, Italy)

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Keywords: Geothermal energy, thermal conductivity, low enthalpy.

Energy is an essential condition for the global growth of a community, as it represents a key element for development of all the anthropic activities. In the last decade, renewable-based systems have been developed for reducing the energy consumption, limiting environmental damages and for achieving maximum incomes with the lowest impact. Recent debates on these issues have led to the construction of a more detailed profile of shallow geothermal resources. In Sicily, geothermal energy can play a key role among renewable sources. Indeed, numerous active volcanoes (e.g. Etna, Aeolian Islands, Pantelleria) or areas at high hydrothermalism (e.g. Paternò, Sciacca, Mazara del Vallo) make large part of the land highly suitable for the exploitation of medium-high enthalpy geothermal resources. Particularly Aeolian Islands are among the most interesting geohydro-thermal sites of Southern Italy, as they offer a large spectrum of geothermal resources from low to medium-high enthalpy. In this study we have focused our attention on the Island of Salina due to the large variety of volcanic terrains, verifying of much the knowledge of the geological characteristics of the ground is essential for the correct sizing of low-grade sourced geothermal systems. The case-study is especially aimed at testing how the lithological s.l. features of rocks can influence the low-enthalpy geothermal potential of an area at a micro-scale. For these purposes, a field survey has been carried out in the area of Santa Marina Salina with collection of several geological data, which provide spatial relationships of the observed lithologies either at the surface or at the shallow subsurface (up to 150 m of depth). Investigations of the petrographic and petrophysic characteristics of the rocks (e.g., type, structure and texture variability, etc.) allowed us to get information on the distribution of thermal conductivity in the subsurface at various depth levels. Our preliminary results deliver important information for the correct interpretation of the most suitable areas and their potential in terms of low-grade ground resources. These data are paramount for a precise planning of high-efficiency technical solutions through vertical closed loop systems that use geothermal probes installed at depths on the order of 100 m.

# Fold-related deformation bands: an analogue of a shallow-burial reservoir from Numidian turbidites of Sicily

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Keywords: Deformation bands, Numidian turbidite system, porosity.

Deformation bands are widely recognized in association with faults (Fossen et al., 2007), but here we examine their relationship to folding. Such structures, together with joints and faults, are generally reported from a variety of stress-field settings (shear, compression, extension). Here, we report deformation bands related to a tight syncline developed in the Miocene Numidian turbidites of Sicily. These porous sandstones, deposited above a growing thrust wedge and then buckled during continued deformation, form subsurface gas reservoirs and are analogues for deepwater systems.

Structural data indicate two distinct populations related to folding: the most prominent and recent structures are NE-SW oriented, whereas an older one is partially obliterated. Multi-disciplinary analyses (petrography, petrophysics, X-ray-microtomography) show a general decrease of porosity in deformation bands with respect to host rock, even though a few shear structures reveal an increase of porosity. The principal deformation mechanisms are grain rotation/sliding (Fossen et al., 2007) and pore-collapse (Aydin et al., 2006), consistent with folding having occurred under low burial conditions. Therefore, our study reveals deformation bands can increase the complexity petrophysical properties of subsurface sandstone reservoirs - not only around fault zones but also across fold structures.

Fossen, H., Schultz, R. A., Shipton, Z. K. & Mair, K. (2007): Deformation bands in sandstone: a review. Journal of the Geological Society, 164(4), 755-769.

# Multi-scale fracture stratigraphy of Lower Cretaceous limestone rocks exposed at the Monte Alpi, southern Italy

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Keywords: Photogrammetry, Fractured carbonates, Discrete Fracture Network modelling.

This work focuses on the control exerted by primary heterogeneities pertaining to the Lower Cretaceous limestones of the Inner Apulian Platform, exposed at the Monte Alpi, southern Italy, on the dimensional and scalar properties of the fracture network that crosscut them. By combining traditional scanline and scanarea methods applied to outcrop-scale fractured volumes with photogrammetric analysis of the reservoir-scale, western cliff of the Monte Alpi, we assess the abutting and crosscutting relationships among bed interfaces, prominent transgressive surfaces and bed-perpendicular fractures. The former elements consist of mm-thick, pressure solution enhanced surfaces, which extend laterally for a few 10's of m and often show amalgamation and bifurcation geometries, whereas the prominent ones are laterally continuous for km's, and consist of up to a few cm-thick, clay-rich levels due to a quick drowning of the platform. Bed-perpendicular fractures are either Strata Bound (SB), compartmentalized within individual limestone beds, or Non Strata Bound (NSB). The final goal of this work is to provide reliable data key for computation of both fracture porosity and equivalent permeability after DFN modelling of geocellular volumes, whose sizes cover the all range of observation scales employed for this work.

Results of field structural analysis show that SB fractures consist of opening-mode fractures, joints, which form two cross-orthogonal sets, bed-perpendicular sets characterized by mutual abutting relationships. NSB fractures consist of sheared joints, which offset a few cm the individual bed interfaces, and often abut against the prominent transgressive surfaces. Outcrop-scale fracture analysis show that both SB fracture sets are characterized by a spacing distribution proportional to the bed thickness, by a negative exponential, multi-scale spacing distribution, and values of coefficient of variation comprised between 0.6 and 1.9. These data point out to a network comprised of two cross-orthogonal, coeval joints sets, which likely formed due to stress relaxation during vertical loading of the limestones, prior to Upper Miocene times. On-going work performed on 3D virtual outcrops, which were obtained by mean of an unmanned aerial vehicle data acquisition, focuses on the dimensional and multi-scale properties of NSB fracture sets. Results of this work will shed lights into the possible role exerted by shear localization along pre-existing SB fractures, rupture of bed interfaces, and coalescence of nearby sheared joints crosscutting adjacent limestone beds on the NSB fracture spacing distribution. Furthermore, these results will be key to also decipher the role played by nearby, through-going fault zones on their development.

# Hypothermal springs of La Calda, Monte Alpi (southern Italy): first results of an integrated hydrogeological and structural study

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Keywords: carbonate aquifer, inverse hydrogeological budget, hypothermal springs.

Hypothermal springs are located along the SW edge of the Monte Alpi massif, southern Italy, which is comprised of Jurassic-Lower Cretaceous carbonates and Upper Miocene mixed carbonate-terrigenous deposits pertaining to the Inner Apulian Platform. All together, the hypothermal spring average discharge is about 0.5 m<sup>3</sup>/s, at a constant temperature of 22-22.5 °C all year-long. The main physico-chemical properties of this hypothermal water belong to the Ca-SO<sub>4</sub> hydrofacies, with a high sulfate concentration. At the Monte Alpi, cold springs are also present, and characterized by very small values of water discharge, which are comprised between 14 \*10<sup>-3</sup> m<sup>3</sup>/s and 1\*10<sup>-4</sup> m<sup>3</sup>/s, and temperatures of 6-12 °C. The main physical-chemical properties of this cold spring water belong to the Ca-HCO<sub>2</sub> hydrofacies. The hydrogeological setting of the Monte Alpi area is hence characterized by shallow water circuits, which localize within the fractured carbonates cropping out away from major fault zones or, alternatively, within the slope debris fans, and deeper circuits fed by meteoric water that infiltrates the major, outcropping, high-angle fault zones. A good understanding of the control exerted by both diffuse and localized deformation on water migration and storage is therefore key to decipher the Monte Alpi hydrogeological setting. To investigate this topic, this work focuses on the inverse hydrogeological budget of the Monte Alpi area. By computing all the available hydrogeological data in a GIS environment, including the results of a year-long hydrogeological monitoring of the cold springs, a conceptual hydrogeological model of the Monte Alpi massif is proposed. This model highlights the modalities of water recharge at surface, through both fractured carbonates and high-angle fault zones, and on the storage of infiltrated meteoric water at depths of 1-2 km. In particular, the average active recharge value was computed for the whole Monte Alpi area, and then compared with the total amount of water discharge from both cold and hypothermal springs. Results are consistent with the Apulian carbonates of the Monte Alpi forming an isolated carbonate aquifer, at depth, dissected by both ENE-WSW and NW-SE high-angle fault zones. The former fault zones bound the massif to the SW, crosscutting both clayish formations of the allochthon and Apulian carbonates, and allow the ascendance of warm waters. Their hydraulic behaviour is interpreted as characterized by a combined conduit-barrier permeability structure, in which the clayish fault cores act as baffles/impermeables for cross-fault fluid flow, whereas the carbonate damage zones as conduits for faultparallel flow. Differently, the NW-SE trending high-angle fault zones crosscut the exposed Apulian carbonates of Monte Alpi, are envisioned as main fluid conduits for water infiltration at depth. Their hydraulic behaviour is hence interpreted as characterized by a diffuse fluid conduit permeability structure.

#### Impact of gravity-driven deposits on fault damage zone architecture

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Keywords: mass transport deposits, carbonates, Gargano Promontory.

The importance of gravity driven mass transport deposits in basinal Carbonates may be overlooked in reservoir prospection due to their sub-seismic scale. However, their presence may have a significant impact on the reservoir quality both in terms of diverse primary porosity (lithological differences), and the development of dissimilar fracture networks within these lithologies with respect to the units of horizontal beds, which may have impact on the fault damage zone architecture. This study documents the variability of both background and fault related fractures (i.e. their distribution, intensity and connectivity) affecting basinal tight carbonates intercalated by gravity-driven deposits in Gargano, Southern Italy. Various types of gravity-driven deposits (slides, coherent slumps, semi-coherent slumps and debris-flow deposits) show different fracture network characteristics with respect to the underlying and overlaying horizontally-bedded units. We documented that the background deformation within coherent slumps is characterized by greater fracture intensity variability (due to the irregular geometries of the folded beds) with respect to the horizontally-bedded units. Meanwhile a noteworthy difference was observed between the debris-flow deposits and horizontal beds. Due to the similar mechanical behavior of these two units, the fracture intensity is controlled by the thickness of the horizontallybedded units and debris-flow deposits. In case of fault damage zones, an important difference in fracture intensity and vertical connectivity occur between the horizontally-bedded units and debris-flow deposits. The horizontally-bedded units are impacted by the preexisted fractures produced by background deformation, meanwhile the debris-flow deposits show higher fracture intensity and connectivity related to the later faulting.

### Preliminary paleothermal and geochemical data of the sedimentary succession in the Huleylan well, Lorestan, Iran

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Keywords: Vitrinite reflectance, X-ray diffraction of clay minerals, Huleylan well.

Rock-Eval pyrolysis, organic petrography and X-ray diffraction of clay minerals are useful techniques that provide information on thermal evolution of sedimentary successions and allow quantifying the maximum burial the rocks underwent. These kinds of information are of primary importance for oil exploration studies because they provide insights on source rock thermal maturity.

The Huleylan well, located in central Lorestan, Iran, intercepts a 3.5 km-thick Cretaceous to Pre-Permian sedimentary succession characterized by shaly limestones, dolostones and evaporites. Lower Cretaceous Garau and Middle Jurassic Sargelu Fms are the source rocks in the Huleylan well feeding carbonate rocks of the Sarvak and Najmah Fms that are sealed by low permeability anhydrite-bearing deposits. Thirty-two cuttings were collected for X-ray diffraction and organic matter optical analyses in order to define the thermal maturity of the sedimentary succession and constrain 1D burial and thermal history of the well. A general increase of organic and inorganic thermal parameters such as vitrinite reflectance and mixed layers illite-smectite (I-S) as a function of stratigraphic age was observed. Vitrinite reflectance values range between 0.67% and 0.86% in the Garau Fm indicating mid-mature stage of hydrocarbon generation up to 1.8% at depths of 3.5 km where Pre-Permian rocks are intercepted. Mixed layers I-S are short-ordered (R1) structures at depths of 650 m and converts into long-range ordered structures (R3) at depths of 800 m. From 800 m up to 3.5 km only R3 structures with decreasing expandable layers are found. The illite content in I-S ranges between 75% to 95% indicating deep diagenetic conditions.

Rock-Eval pyrolysis data provided by National Iranian Oil Company belong to the Garau and Sargelu Fms. TOC values in the Garau Fm at depths of 752 to 1197 m range from 0.48 to 1.68 wt.%. In the Sargelu Fm, TOC value is 4.5 wt.% at depth of 1274 m.  $T_{max}$  values in the Garau Fm range from 433 to 461 °C whereas they are about 446-448 °C in the Sargelu Fm indicating early to mid-mature stages of hydrocarbon generation.  $T_{max}$  data and low hydrogen index values (<130 mgHC/gTOC) for both formations exibit kerogen type III.

1D thermal modeling of the sedimentary succession in the Huleylan well suggests that the Garau and Sargelu source rocks experienced a lithostatic load of 3.4 and 4.2 km respectively during the late Miocene. Since the Late Miocene erosion removed about 2.95 km of sediments.

### Tectonic control on bauxite formation during Upper Cretaceous faulting of the Outer Apulian Platform

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Keywords: Syn-sedimentary faulting, Bari Formation, Altamura Formation.

The study aims at reconstructing the control exerted by syn-sedimentary, extensional faults on formation of the canyon-filling bauxite deposit cropping out at Spinazzola (BAT), southern Italy. There, a ca. 25 m-thick, Turonian age, bauxite deposit is placed in between the topmost portion of the Valanginian-Cenomanian Bari Fm. and the bottom of the Coniacian-Early Campanian Altamura Fm. The bauxite deposit marks therefore a ca.  $4 \pm 1.8$  My-long depositional hiatus. This deposit is a homogeneous rock volume comprised of Fe and Al oxides and hydroxides and originated from allochtonous mafic igneous protoliths. It recorded three humidity fluctuations as shown by Ce anomalies documented across the Spinazzola deposit. The bauxite accumulated at the hanging-wall of syn-sedimentary, NW-SE striking extensional faults, forming a horst and graben geometry crosscut by an orthogonal, conjugate fault system.

In this work, we performed detailed structural analyses of the Turonian, syn-sedimentary fault network, petrographic characterization of limestone samples collected both at the top and at the bottom of the bauxite deposit, XRD analysis of bauxite powder samples collected along transects across this deposit, and SEM investigation of the mm-sized, accretion ooids it includes. In the field, we paid a particular attention to the bauxite cropping out in proximity of the faults, to the debris-filled paleo-sinkholes and to the bauxite-filled open fractures sub-parallel to the main fault sets.

Preliminary results of field structural analysis and petrographic characterization show that basal limestone is moderately to severely affect by karst; top limestone onlaps to SW on fault surfaces; bauxite shows an internal angular unconformity, gradually disappearing, due to syn-sedimentary activity of normal faults. Limestone shows four sedimentary facies forming a shallowing upward sequence, which sectors are dislocated and put contiguously by a strike-slip right-lateral fault.

Ongoing XRD and SEM-EDS analyses will elucidate about possible variations of both texture and mineralogy of the study bauxite, which might clarify about possible effects of syn-sedimentary slip along the bounding extensional faults on its diagenetic evolution. Furthermore, detailed analysis of clay minerals present within the bauxite deposits will better explain on the possible role played by the paleo-phreatic level on bauxite formation. Finally, detailed analysis of the dimension of accretion ooids will likely provide useful information on the possible cycles of dry and wet climate periods. In fact, previous work documented that the sub-circular ooids are made up of alternations of boehmite and Al-hematite layers, which reflect alternating wet tropical and drier conditions.

These results will be beneficial for planning and extraction in mining activities, thanks to a high-resolution methodology for structural characterization of an ore deposit.

#### Fault seal analysis as tool to reduce the uncertainties in E&P - Science or fiction?

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Keywords: Fault seal, fault zone, subusrface.

Faults are important structures in the exploration and production of hydrocarbon because they exert significant control on the migration, entrapment, and subsequent compartmentalization of hydrocarbons. The effect of faults on the flow of hydrocarbon can be complex: whereas some faults allow fluid flow across them, others do not, causing various complications in hydrocarbons reservoirs. To improve the efficiency in exploration and development of hydrocarbon reservoirs, it is imperative to understand the distribution of faults, to depict their internal geometry and 3D pattern, and to estimate the petrophysical property of the associated fault rock.

The prediction of fault retention capacities in static conditions is a well established and tested methodology. However, the exercise of comparing a column predicted by this method and the actual result from drilling is seldom done. One of the reasons for this is that once the study on retention capacity is done, several years can go by before the prospect is drilled.

The main objective of this study was to test the methodology of retention capacity by capillary sealing. In order to accomplish this, five in-house prospects compartmentalized by faults already drilled by several exploration-appraisal wells have been studied simulating, as good as possible, the original exploration conditions before drilling.

The predictions of the fault retention capacity study are coherent with the well results, thus proving the reliability of the methodology. The study of the faults retention capacity highlighted that the degree of structural complexity is certainly the most important parameter in the prediction of fault sealing capacity. For multi-phase faults with a complex tectonic history, uncertainties and approximations related to the workflow cannot be compensated by the quality of the data and the sedimentological properties neither. The quantitative predictions become more reliable when a more refined stratigraphic knowledge of the reservoir is incorporated into the prediction process.

Our results suggest that for complexly faulted reservoirs, the architecture of the fault zone plays a role. Complex fault zones have a higher probability of sand and shale "smear" providing cross-fault fluid pathways. A key control in fault zone architecture is the mechanical vertical heterogeneity not the stratigraphic heterogeneity. In this context, outcrop analogues can provide essential constraints for the understanding of the hydraulic behavior of faults in subsurface hydrocarbon reservoirs.

# Geological and numerical fluid dynamic modeling of the offshore hydrocarbon reservoir of Santa Maria Mare (central Adriatic Sea)

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Keywords: Oil and Gas Reservoir, 3D numerical modeling, seismicity.

The study shows the results of a geological and numerical modeling of Santa Maria Mare (SMM) offshore hydrocarbon reservoir (central Adriatic Sea) discovered in 1974. The field refers to B.C 7.LF concession that covers 201 km<sup>2</sup> and a set of 13 deep wells were drilled and several different logs acquired; the maximum depth of wells is around 3 kilometers and some seismic reflection surveys have been realized. The hydrocarbons production from the reservoir began in 1975.

The geological domain of the reservoir refers to the well-known *Umbro-Marchigiana Series* and hydrocarbon mineralization is inside the *Scaglia Calcarea Bianca-Rossa Formation* divided in impermeable inter-reservoirs and permeable reservoirs (called IR1, R1, IR2, R2, IR3, R3, IR4, R4) with medium thickness between 20 m (IR2) and 90 m (R3). The inter-reservoirs are characterized by the absence of turbidities that in some reservoir situation show a metric dimension and are well separated.

The meticulous analysis of all the available data led to realize a detailed 3D geological static model and then a fluid dynamic model has been implemented to study the over thirty years old history of hydrocarbon production considering the petrophysical proprieties of the referring geological formations. The production history of natural gas and oil covers relevant timeframes and respectively of 26 and 34 years with an annual oil medium production of 177000 tons between 1980-2015 and 28000 10<sup>3</sup> Sm<sup>3</sup> of gas between 1980-2015. Studies of the dynamic parameters and the historical production have shown that the reservoir is characterized by an excellent maintenance of the pressure due to the raising of the water table. The numerical modeling has also considered the injection of formation waters produced during the SMM field exploitation and the ones coming from other hydrocarbon reservoirs; a total amount of 4390 km<sup>3</sup> of formation waters have been re-injected between 1975-2015 and 3090 km<sup>3</sup> belong to Santa Maria Mare reservoir.

The results obtained by the fluid dynamic modelling process were more than satisfactory with a very slight differences between the calculated values of pressure and the ones measured during the exploitation of the field.

A particular analysis has been made for the period March-September 1987; indeed, in March a peak of formation waters injection has been reached followed in September by some earthquakes with local magnitude of 5.0 and epicentral area located 5-6 km East from SMM reservoir. The analysis of the pressure field linked to the peak shows that the alterations to the natural pressure field are limited to restricted volumes very closed to the 4 wells used for re-injection and damped in a few hundred meters. As a consequence it is highly unlikely that the re-injection of formation waters could have triggered the earthquakes of September 1987.

### Lower Pleistocene large-scale tidal architectures investigated using remote techniques (Siderno Basin, Calabria) to improve reservoir modelling

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Keywords: Tidal sand bodies, Reservoir, LIDAR.

Ancient tidal sand bodies accumulated in shelf settings represent a productive type hydrocarbon reservoir. Tidal sand bodies often exhibit elongate shapes and thickness under the minimum resolvable seismic resolution. Their internal features are thus difficult to be properly assessed in seismic and modelling is often hampered by a number of uncertainties. When detected in outcrop, analogue deposits are therefore crucial and their facies reconstruction is key in support of reservoir characterizations.

The early Pleistocene exposed in the Siderno Basin (Southern Italy) includes ~80-m-thick fine sands and marls erosionally overlying by ~60-m-thick biocalcarenites (Mt Narbone Fm; *cf*. Cavazza et al., 1997). This latter unit internally exhibits multiple cross-cutting sets, trough and tabular cross strata, angular to tangential foresets and plain-parallel lamination, which are physical attributes recording the migration of extensive bedform fields in a paleo strait dominated by amplified tidal currents (Colella & D'Alessandro, 1988; Longhitano et al., 2012; Rossi et al., 2017).

Tidal biocalcarenites are exposed in up to 3 km long, 100 m wide sand bodies, many of which are rarely accessible for detailed analysis and the use of remote-sensing techniques integrating conventional facies analysis is required.

In this study, we present the preliminary results of a LIDAR Scan acquisition and a high-resolution photograph analysis on one of the best exposed outcrop of this tidal succession. Our investigation reveals major hierarchical bounding surfaces, separating a number of different facies distinguished based on their internal geometries. These architectures are believed to reflect different energetic stages of the tidal currents during sedimentation.

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# Structural control on oil first migration within Triassic shale, Favignana Island, Italy

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Keywords: Structural diagenesis, First migration, Fracture network.

Fluid migration in rocks characterized by low values of primary porosity and permeability can be affected by fractures, whose formation is strongly influenced by the diagenetical history of the host rock. The aim of this study is to define the role of fracture networks on oil first migration within outcropping Triassic carbonatic shales exposed in the northernmost sector of Favignana Island, which can be considered as potential source rock in offoshore western Sicily. The study outcrops are located along the limbs and the nucleous of a syncline that formed during Miocene with a N50E trending fold axis. The ouctrops show cm- to m-thick beds of yellowish clayey marls and marls, which are alternated to thick beds of grayish to blackish stromatolitic and loferitic limestones. This study is based on the integration of geological, structural, sedimentological and microstructural studies with chathodoluminescence and Scanning Electron Microscopy (SEM) analyses. The goal is to constrain both relative timing of deformation and chemistry of the detected organic matter. Preliminary field results highligt presence of three sets of high-angle to bedding and one sets of low-angle to bedding opening mode fractures made up of joints and calcite filled, syntaxial veins. They formed during different episodes, in which the pre-existing sets were sheared forming tensile fractures at their extensional quadrants. Analysis of thin sections in transmitted light allowed recognition of several bed parallel catagenetic micro-fractures. Genesis of this kind of structures was related to the increased oil volume due to organic matter maturation. The recurrent evidences of oil in the central part of veins related to the earlier sets suggest that these were the only fracture sets that were formed during oil migration. Moreover, SEM microanalysis highlights the presence of S, Na, Cl and Sr inside the vein hosting the organic matter. Cathodoluminescence measurement observations show different brightness degrees in both the analysed vein mineralizations and in their host rocks; in particular, more than one set of veins shows different mineralization phases while other are characterized by the same brightness degree of their hosting rocks. Data and interpretation carried out during this ongoing work provide the first evidence of structurally driven oil first migration in the Aegadian Islands.

# Investigating subsurface basin architecture from the sky with UAV-based Structure from Motion Photogrammetry: an example from the Calvello Basin, Southern Italy

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Keywords: Hydrocarbon exploration, 3D geo-models, southern Apennines.

Hydrocarbon exploration in fold and thrust belts is characterized by a high degree of geometrical uncertainty due to poor seismic quality and, often, availability. The identification and evaluation of hydrocarbon traps are strongly related to deep-seated faults compartmentalizing the reservoir and individuating the main prospective structural compartments. Deep-seated and thick-skinned structures could also control the presence and the style of tectono-stratigraphic architecture of thrust-top basins.

This current research demonstrates the use of UAV-based Structure from Motion photogrammetry (SfM) to investigate the stratigraphic and structural style of the Plio-Pleistocene thrust top Calvello basin in the southern Apennines lying near-by the Tempa Rossa oilfield.

The Calvello Basin is one of several Plio-Pliestocene basins along the axial portion of the Apennine chain which bury deeper structures of the chain thrust system. These basins contain thick deformed successions of marine to continental syn-tectonic sedimentary strata which record the spatial and temporal tectonic evolution of the southern Apennines, including the quaternary strike-slip and extensional tectonic phases. Given the vertical position over the hydrocarbon producing units of the buried Apulian Platform, this basin has been selected to apply and test a new method in order to unravel the interplays between deep-seated faults affecting the reservoir quality and their role in controlling basin evolution and architecture.

The use of this new method, calibrated with new age dating constraints of marine successions and field mapping, will allow the creation of well-constrained 3D basin models, incorporating high-resolution stratigraphic and structural details. The 3D geo-models will be used to constrain subsurface interpretations creating a bridge between regional tectonic conceptual models and field-based observations.

# Mechanical stratigraphy and structural controls on permeability across fault zones

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Keywords: fault zone, fractured reservoir, fluids migration.

It is well known that fracture distribution and fault zone architecture play a significant role in the containment and migration of fluids in natural fractured reservoirs. Although only faults with a throw larger than 15 m are detectible in seismic images, understanding fluid flow characteristics in below seismic scale resolution faults is imperative when correctly predicting the productivity of a geofluid reservoir. Fracture propagation is strictly related to the lithological and relative mechanical properties of rocks. For this reason, heterolithic beds in siliciclastic rocks provide a unique opportunity to study how reservoir properties (porosity, permeability) change across a fault zone, depending on mechanically different stratigraphic layers that undergo the same deformation behavior. In this study, we have chosen two heterolithic successions: 1) the Miocene Cilento group, located in southern Italy in the Campania Region, and 2) the Miocene - late Oligocene Macigno formation, which outcrops in southern Tuscany. Sediments of the the Cilento group are generally made up of sandstone-pelitic and marly-calcarenite turbidites, with conglomerate intervals deposited unevenly throughout the section in thin and medium layers. The Macigno succession is represented by siliciclastic turbiditic sandstones with minor siltstones, mudstones and shales that are evenly distributed throughout the section. A comprehensive study of the two localities will provide an analogue of the changing permeability based on mechanical stratigraphy, fault core development, and fracture propagation throughout the section, in varying bed spacing and lithologies from initial nucleation to well-developed fault systems in both evenly and unevenly distributed heterolithic beds. Thickness, lithology and character of the sedimentary layers (evenly vs. unevenly distributed layers) govern fracture density and propagation, as well as permeability changes in within a single bed.

#### The effect of tides on morphology, stratigraphic architecture and sediment bypass in river-dominated deltas

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Keywords: Tide-influenced deltas, compound clinoforms, Delft3D.

Deltas are dynamic and sensitive systems that undergo changes of morphology, channel network, and stratigraphic architecture in response to variations in coastal processes, e.g., waves and tides. These changes need to be properly understood in order to make reliable subsurface predictions.

Single coastal process dominance has been studied extensively using numerical modeling methods, but the sensitivity of deltas to mixed-process environments has rarely been examined. Therefore reservoir predictions based on such models could be highly misleading when used in mixed-process delta systems, where laterally varying waves and/or tidal processes can rework the deposits of fluvial floods. This study aims to bridge this gap of knowledge by investigating the influence of tidal currents on river-dominated deltas in terms of deltaic stratigraphic architecture and sediment partitioning using Delft3D. We conducted 24 modeling runs with different ranges of tidal amplitude and initial sediment composition of the substrate.

The modeling results show that deltas formed under pure river-dominated conditions have a concave deltafront profile while with increasing tidal amplitude the delta front becomes convex and develops a compound clinoform geometry. With no tidal currents, distributary channels avulse and bifurcate frequently, resulting in the complete reworking of deltaic lobes. As a result, coarse sediment is stored in the proximal delta plain. In contrast, the presence of strong tidal currents creates deeper and stable distributary channels. These channels do not rework previously deposited deltaic lobes, but act as an efficient conduit for sediment to bypass across the delta during ebb currents. Furthermore, the analysis of sediment fluxes across the delta shows that ebb tidal currents increase suspended and bedload sediment fluxes by at least 3 times compared to cases without tidal currents. The enhanced sediment flux leads to deposits with net-to-gross ratios higher in tidally-influenced cases than in their river-dominated counterparts.

This study shows how tidal currents, even under river-dominated conditions, have strong effects on delta surface morphology, stratigraphic architecture, and sediment partitioning. In particular, channel overdeepening and compound clinoform geometries are possible important tidal signatures that should be considered when interpreting ancient systems. These features are critical for the modeling of petroleum plays as they are key elements in reservoir architecture and migration pathways. Furthermore, this study shows that sand may be bypassed much farther basinward in tide-influenced than in purely river-dominated deltas, contrary to common assumptions about net-to-gross distribution.

### Estimation of VP-VS, density, elastic moduli and thermal conductivity of Messinian Salt Rocks, Sicily: important physical parameters for multiple purposes

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Keywords: Messinian evaporites, Salt Rock, Halite.

The Messinian salinity crisis led to deposition of kilometer-thick sequences of evaporites along in the deep basins of the Mediterranean Sea during the Late Miocene (5.96-5.33 Ma). In Sicily, Messinian evaporites of Gruppo Gessoso Solfifero cover an extended area for more than 1000 km<sup>2</sup>. In particular, previous authors have established that halite accumulations achieved thicknesses of ~1 km within the Caltanissetta Basin (central-southern sector of Sicily).

Although petrophysical analyses of salt samples are infrequent in literature, their characterization arouses extensive interest for several utilities, such as for understanding the mechanical behavior at different T and P conditions, as well as for hydrocarbon exploration and for storage. Therefore, this work provides the first detailed description of physical and mechanical properties of Messinian halite from Sicily.

For the purpose of this, a set of 28 specimens of Messinian halite were sampled in a Sicilian mine (Italkali) has been analyzed and tested using different tools. Ultrasound velocities (P and S) measured under hydrostatic confining pressure up to 100MPa, range between 4200 - 4800 m/s and 2500 - 2700 m/s respectively. From Gas-porosimeter measurements, low porosity and negligible permeability of the samples demonstrated the weak presence of pores and the totally non-interconnection among them, endorsing the non-permeability of the typical salt rock units. Density has been estimated using a Helium pycnometer with halite showing low density characterized by values of 2.1 to 2.2 g/cm<sup>3</sup>. Elastic properties such as Young's modulus, shear modulus, bulk modulus and Poisson's ratio were computed from velocity values of P- and S- waves and density. Lastly, we investigated on thermal conductivity of halite obtaining high values of about 6.5 W/m°K at the temperature between 19.0 and 21.8 °C.

By virtue of results achieved, this work will contribute to supply basic information about salt characteristics: physical and mechanical parameters will result useful for new possible implications.

#### Sedimentological Data Integration in a Process-based Approach for Reservoir Model

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Keywords: Process-based model, sedimentology integration, green field.

The global uncertainty in deep-water green fields and fields under early development is very challenging in its estimation and integration.

Among the main uncertainties, the sedimentological model and the architectures of the geological bodies have a relevant role in the evaluation of the field potential and of the field development plan.

As a consequence, the scope of this work is the direct quantitative integration of the sedimentological/ depositional uncertainty through the creation of a suitable number of different scenarios.

A process-based methodology was chosen in order to generate realistic scenarios using Flumy software. It allows generating many different 3D sedimentological models with a great geological realism.

The variability among the created scenarios included the missing information about the field. For example, one might include high sinuosity channels in a very sandy setting. On the other hand, another one might present low sinuosity channels in a low sandy setting.

Every scenario is a quantitative 3D model, which can be imported to condition the facies and petro-physical properties distribution. Therefore, the simulation improves the geological detail and gives a sedimentological meaning to the whole model.

This methodology has been successfully applied to an African deep-water reservoir, for which several 3D sedimentological process-based models have been generated and considered in the field appraisal during development.

The advantages are multiple. Especially in case of low quality seismic, the different scenarios capture the geological heterogeneity and reconstruct different reservoir architectures also in the area located away from the drilled wells. As new data become available (i.e. high quality seismic, drilled wells, dynamic data), the different scenarios will be validated according to their consistency to the novel datum.

Thus, the models that are no more consistent with the current dataset are simply discarded.

Then, the consistent sedimentological models were used as EOD (Environment Of Deposition) during the reservoir facies and petrophysics distribution phase, mainly relying on traditional geostatistical algorithms.

The combination of EOD and traditional geostatistical algorithms allowed constraining both the reservoir facies and the petrophysics to the different sedimentological hypotheses and preserve the depositional and geological consistency.

The whole methodology allowed assessing the sedimentological uncertainty in a poor dataset setting through the construction of different scenarios. Moreover, the sedimentological constrain is no more a conceptual model coming from a 2D sketch or map but it is a quantitative 3D model directly integrated in the modeling phase.

Indeed, the process-based models rely on strong quantitative physical laws during the simulation of the geological bodies. Flumy models return the EODs, which have a strong sedimentological significance, and different sand percentages among the scenarios.

#### Miocene outcrop analogues for the Upper Jurassic Rogn Fm in the Norwegian Shelf

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Keywords: Outcrop analogue, current-dominated sedimentation, Sardinian Seaway.

The Upper Jurassic Rogn Fm represents one of the major reservoir of the Norwegian Shelf (NS). This sandrich succession is up to 50 m thick, coarsening upward and diffusely cross bedded. Sourced from the erosion of crystalline basement highs, it accumulated in embayments and shelf environments. The distinctive cross bedding suggests the dominance of traction currents during the deposition in both the reconstructed settings. However, due to thicknesses below seismic resolution and a limited number of well cores, there are still uncertainties on its depositional settings that may be reduced by using appropriate outcrop-analogues.

The tectonic setting and the stratigraphic history of discrete parts of the NS during the Late Jurassic suggest similarities with the Miocene of the Sardinia (Italy). Based on this potential correspondence and on resemblances provided by spectral-decomposition images, two field areas have been selected as potential outcrop analogues.

The first study area bears good similitudes with the Rogn sandstone accumulated in coastal embayments. Aquitanian-Burdigalian, ~140-m-thick, transgressive sandstone to marl deposits lap against the flank of a crystalline basement block. Twenty-m-thick basal conglomerates and cross-bedded sandstone, record fluvio-deltaic channels, mouth bars and floodplains initially filling an incised valley. These deposits are transgressively overlain by heterolithic, tidal sandstone and mudstone, forming subtidal to intertidal bars and channels accumulated in a barred tidal flat. About 50-m-thick beach-barrier sandstone and shelf marls, recording a late phase of major transgression, seal this succession. The tidal signal in the heterolithic cross strata reflects the onset of a tidal influence, possibly related to the presence of an adjacent wider, current-dominated seaway (i.e., the Sardinian Seaway).

The second study area, a half-graben of the northern Sardinia, suggests analogies with the Rogn Fm deposited in a shelf setting. Serravallian, 50-250-m-thick sand bodies lie adjacently to the basin margins or occupy elongate depocenters in axial sectors of the basin. These deposits are dominantly siliciclastic and exhibits a variety of different scales of cross bedding, interpreted as the effect of the influence of alongshore (tidal) currents on delta-front areas and promoting the migration of bedforms in shelf basinal sectors.

Both the presented field areas provide new insights for the interpretative revision of many Rogn reservoirs of the NS and constrain the reconstruction of the Miocene Sardinian Seaway in the western Mediterranean.

#### From fracture analysis to fluid flow evaluation of fractured carbonates

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Keywords: Deformed Carbonates, Fracture analysis, Geological Model.

This work assesses the impact of the stratigraphic and structural heterogeneities on the fluid distribution and migration within a fractured carbonate reservoir analogue. The study was carried out in the abandoned Roman Valley quarry (Majella Mountain, central Italy), well-known for its historical bitumen extraction. The studied rocks consist of ramp carbonates of the lower member of the Bolognano Formation (Oligocene-Miocene in age) mainly composed of grainstones, and secondary packstones and wackestones. In the quarry, the exposed rocks are crosscut by two high-angle oblique-slip faults striking WNW-ESE with up to 40 meters of throw.

Laboratory measurements and very detailed Discrete Fracture Network (DFN) models are integrated to quantify matrix and fracture contribution to porosity and permeability within each of the lithofacies cropping out in the study area. DFN models (cubes with 4-meters per side) were constrained by spatial and dimensional properties of fractures obtained by scanline surveys. DFN models provide a robust prediction of flow characteristics but due to their complexity and size, DFN models are often unsuitable for field-scale predictions. This work describes sensitivity analysis on fracture effective properties and a Representative Elementary Volume (REV) analysis aimed at constrain the uncertainty in fractured reservoir modelling. These models, calibrated with the field observations, were used to calculate fracture permeability and porosity based on the Oda upscaling method.

Finally, the obtained reservoir properties were used to build an outcrop-scale static model of both the matrix and the fractures, accounting for their stratigraphic and structural heterogeneities. The results are more consistent with field observation of bitumen distribution for the matrix component respect to the fracture one. This model can be used as input to dual porosity-dual permeability flow simulations to test fluid pathways for various flow scenarios in order to reduce uncertainties on both productivity and sustainability of geofluids in fractured carbonate reservoirs.

# Assessment of the fracture roughness and their control on single fracture permeability in carbonates

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Keywords: Fracture permeability, fracture roughness, carbonates.

Fractures play a key role in fluids migration and storage in the upper crust. Fluid flow through a single open fracture has been traditionally described by the cubic law, which is derived from the Navier-Stokes equation for the flow of an incompressible fluid between two smooth-parallel plates. Thus, the permeability of a single fracture depends only on a theoretical aperture value, the so-called hydraulic, which differs from the mechanical aperture (the measure of separation between the joint wall surfaces). Numerous works have included a friction factor in the permeability equation of individual fractures or derived a hydraulic aperture based on the fracture walls roughness. In field-based studies focused on fracture modelling, it is a common methodology to derive the hydraulic aperture from the mechanical aperture and a measure of roughness (e.g. joint roughness coefficient). It is expected that the fracture aperture and roughness will depend on the type of fracture itself (e.g. joint, pressure solution seems, sheared fractures) and the textural properties (e.g. grain/ pore size distribution, specific surface area) of the host rock. The mismatch between both walls of the fracture, caused by displacement or diagenesis, is also a crucial element to be considered especially at the reservoir conditions. Despite these considerations, fracture aperture and the surface roughness remain among the most imprecisely evaluated fracture property in reservoir characterization.

In this work, a new methodology for quantitatively assessing fracture wall surface topography and its control on permeability and hydraulic aperture of single fractures is presented. This approach consists of combining Structure from Motion photogrammetry, performed in situ on outcrop fracture surfaces or in laboratory facilities, thin section analysis, fracture topography spectral analysis, single synthetic fracture modelling, and flow simulations using the lattice-Boltzmann method. This method is applied to widely studied hydrocarbon-bearing middle- to outer-ramp carbonate rocks exposed in central Italy (Maiella Mt.). To widen the results, multiple facies, including wackestones, mudstones, packstones and grainstones, were analyzed. Similarly, different mechanical aperture, mismatch values and displacement scenarios of the fracture walls are assessed in the simulations to evaluate their control of permeability.

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# **Session S13**

# **Outcrop analogues in exploration and production**

Conveners And CHAIRPERSONS Domenico Chiarella (Royal Holloway, University of London) Massimo Rossi (ENI)

# Interaction between hydrothermal-carbonate precipitation and volcanoclastic sedimentation in continental settings: is there any relevance to hydrocarbon generation?

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Keywords: travertine, volcanoclastics, hydrocarbons.

With the discovery of giant South Atlantic hydrocarbon reservoirs, spring-related calcium carbonate precipitation in continental settings has received significant attention in recent years. This has led to the recognition that there is paucity of data concerning the depositional and diagenetic processes and products of these non-marine carbonates, when confronted with the knowledge and vast information available for the marine counterpart. In addition, the interaction of these peculiar deposits with volcaniclastic sedimentation has never been deeply investigated.

In view of all the above findings, a multidisciplinary and multi-scale investigation on fossil hydrothermal spring travertine deposits located in Central Italy, have been conducted. The integrated approach of this research was essentially based on stratigraphic, sedimentary, petrographic, geochemical, mineralogical principles, with significant attention dedicate to petrophysical properties of the studied non-marine carbonates.

The travertine deposit exhibits an articulate range of geo-body types characterized by complex architectural and facies patterns with extensive vertical (from 5 to 20 m) and lateral variation (up to 300m). A large variety of depositional and diagenetic fabric types have been characterized and classified using classical carbonate terminology. The individuated fabric types reflect the precipitation processes due to interplay between abiotic and biotic (i.e., biologically induced by microbial metabolic process or simply influenced by nucleation on microbial biofilm substrate) and/or a combination of both processes, which are subsequently modified by diagenesis. All the above processes largely influence the fabric types petrophysical proprieties. Evaluation of porosity and permeability conducted on selected samples suggests that travertine may represent good reservoir quality rocks.

Another important topic established by this work has resulted in the dedication of significant attention to the relationship between hydrothermal travertine and volcaniclastic sequences, and their potential role in reservoir formation. Volcaniclastics were emplaced during different volcanic manifestations and show typical features of hot emplacement. Petrography and SEM-EDS analysis reveal that primary volcanic characteristics, such as volcanic textures, have been deeply modified by the continuous hydrothermal flowing water, resulting in the alteration of the primary petrophysical characteristics of the deposits. Volcanic activity also influenced the precipitation of unusual travertine fabrics enriched in organic matter, showing evidences of first stage of hydrocarbon generation.

All the above results represent a breakthrough in the coupling between reservoir modelling and the study of geological analogues, giving feedbacks that can favour a better understanding of non-marine carbonate reservoirs.

# Turbidite Sedimentation in the Miocene Foredeep of the Southern Apennines: High Resolution Physical Stratigraphy and Facies Analysis of the Serra Palazzo Formation (Basilicata, Southern Italy)

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Keywords: Southern Apennines, Serra Palazzo Formation, foredeep turbidite system.

The Serra Palazzo Formation, originally defined by Selli (1962), is a siliciclastic and calciclastic turbidite succession of the late Burdigalian-Serravallian (Gallicchio & Maiorano, 1999). It was deposited in the Miocene foredeep of the growing Southern Apennines (e.g. Pescatore & Senatore, 1986), and at the present time it outcrops along the outer margin of this chain. Detailed lithostratigraphic and sedimentological study of the Serra Palazzo Fm. was undertaken in the outcrop type-area of the succession, along the Forluso stream (NE of Campomaggiore, Basilicata, southern Italy), by combining geological mapping and bed-by-bed sedimentary logging. The sedimentary logs span a portion of the Serra Palazzo Formation about 500 m thick along a transect 3,5 km long parallel to the average palaeoflow. The succession is made up of different bed types including: (1) lenticular sand to small pebble grain-size beds; (2) white calcilutites to fine calcarenites, (3) siltstones to very fine sandstones almost always laminated, (4) grey marls, (5) rare beds containing an intermediate division ranging from mud clasts-rich sandstone to muddy sandstone with organic matter and/or mud clasts. These beds are vertically stacked to form various packages made up of: (i) mostly beds 1, (ii) alternations of beds 1-4, (iii) alternations of beds 2, 3 and 4. A graded bed over 20 meter thick ranging from coarse-grained sediment at the base to fine-grained sediment at the top was identified and used as key bed to help log correlation. The succession is characterized by an overall fining upward trend. Preliminary results of sedimentary facies analysis suggest: (i) sediment transport mechanisms range from hyper-concentrated to turbidity flows (Mulder & Alexander, 2001) (ii) facies assemblages are related to different architectural elements, among which channel-lobe transition, channel, levee and overbank. The study aims to provide a detailed reconstruction of the facies assemblage, architectural elements and depositional sub-environments of a foredeep turbidite system from an outcrop perspective and to compare it with other systems in different settings, for example the turbidite system of the Gorgoglione Flysch Fm., deposited in a Miocene thrust-top basin of the Southern Apennines.

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# Tectono-stratigraphic, sedimentological and paleo-oceanographic implications of gateways: insight from southern Italy

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Keywords: paleostraits, onshore and offshore analysis, southern Italy.

Gateways (e.g. straits; seaways, etc.) and adjacent submarine areas represent unique physiographic domains characterised by specific oceanographic processes controlling both erosional and depositional features. Geological studies and geophysical investigations have pointed out as gateways may correspond with morphologically confined basins or block-faulted compartments, hosting unpredictable sediment routings in association with variable tectonic accommodation. In such settings, both bottom currents and associated oceanographic processes (e.g., overflows, tides, waves, eddies, etc.) and morphological constraints can result in sedimentation that departs from conventional sedimentary models and stratigraphic schemes. Consequently, analysis of such settings in the subsurface is often problematic affecting, for example, predictions for hydrocarbon reservoir characterization. Accordingly, presence and distribution of sand-rich deposits is a key risk. Uncertainties can be reduced by studying outcrops and subsurface analogues using facies analysis and seismic interpretations. In addition to these standard approaches, the sedimentary architecture analysis of the outcrops can be performed by using virtual outcrop data (i.e. photogrammetry and LIDAR). Virtual outcrops allow filling the gap between facies and seismic scales in a 3D environment and have the advantages of: (i) analysing outcrops, completely or partially inaccessible; (ii) obtaining a larger and more representative number of measurements; and (iii) being an effective space of fusion with other geological information in order to make more robust estimations. In the present study, preliminary results coming from the onshore and offshore analysis of the southern Italy paleostraits are presented.

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### From 3D virtual outcrops to numerical reservoir models: an integrated approach that brings outcrops to the office

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Keywords: 3D digital outcrops, modelling workflow, reservoir models.

During past decades, progress in computer sciences has enabled to reconstruct very realistic digital outcrop models which are used as analogues for subsurface sedimentary systems, and integrated in the whole chain of characterization and modelling of subsurface reservoirs. Digital outcrops provide useful information about geobody sizes, geometries and connectivity. The interest in outcrop analogues was recently renewed thanks to the development of high-tech virtual outcrop methodologies (Hodgetts, 2013; Schmitz et al., 2014).

There are many advantages in the specific techniques developed for data acquisition from outcrop: continuous collection of data from otherwise inaccessible areas, access to different view angles, increase in possible measurements, attribute analysis, fast data collection rate, and eventually training and communication. These various data are analysed to characterize the spatial distributions of properties, and makes possible to build 3D numerical geomodels at the reservoir scale. They yield likely representations of subsurface reservoirs.

Modelling workflows have been designed to model reservoir geometries and properties from 3D outcrop data, including geostatistical modelling and fluid flow simulations. The data collected from these 3D digital outcrop models provide realistic values for computing the spatial distribution of the geological properties (facies, fracture, erosions, diagenesis, etc...). The numerical reservoir simulations based upon the 3D digital outcrop interpretations are constrained by the extracted geotagged data interpreted from the digital outcrop, and guide the numerical reservoir simulation process. The extraction of such a database is based on an upstream characterization coupling petrographic, sedimentological, structural, diagenetic and petro-acoustic studies.

This workflow is illustrated through two case studies:

- A case study on a turbidite reservoir analogue (Ainsa, Spain) that aims at comparing reservoir models built with conventional data set (1D pseudowells), and reservoir model built from 3D outcrop data directly used to constrain the reservoir architecture;
- A second case study concerns the distribution of microbialites within the presalt lacustrine reservoir analogue of the (Yacoraite Fm, Argentina), where 5 outcrops were modelled and interpreted in terms of facies, and petrophysics, and used to constrain numerical simulations.

In parallel digital technology has changed the way of communicating and transmitting information by introducing these new technologies. This knowledge capitalized by academy or company experts is generally transmitted via field-trips and field trainings whose attendance is generally limited because of costs considerations. There is today a real need to find new ways to capture outcrop analogue information and ease its integration of in our subsurface models. Virtual field trips allow professionals and students to get access and analyze reference outcrops located in distant or inaccessible areas.

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# 3D model of a km-scale outcrop analogue of fractured hydrocarbon reservoirs: the Gozo Island

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Keywords: Outcrop analogues, fractured reservoir, 3D geo-model.

Outcrop analogues have an important role in hydrocarbon exploration and reservoir characterization because they can help filling the gap between seismic and borehole scale. In this work, we present results from our project in the Gozo Island (Maltese Archipelago). Here, a Late Oligocene-Early Messinian carbonatic sequence, composed by different types of carbonates, was affected by two main extensional tectonic events leading to the formation of a complex fracture pattern: i) E-W extension during the Aquitanian ii) N-S extension from the Middle Miocene onwards. We have reconstructed a 3D geological model covering all the Gozo Island (15 x 8 km) using detailed geological maps and borehole data. The geological model has been populated with data regarding the distribution of fracture networks (from photogrammetric DOMs), mechanical stratigraphy and petrophysics using different geostatistical approaches.

#### Slope Failures and MTDs along a Cretaceous Escarpment in Western Sicily (Italy)

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Keywords: MTD, Cretaceous, Carbonate Slope.

In the last decades, many contributions have examined the Mass Transport Deposits (MTDs) in both modern and ancient examples for the comprehension of the sedimentary dynamics along carbonate escarpments. Such sedimentary bodies have a great economic significance, since they are widely considered prone to the development of petroleum systems. In particular, MTDs from Cretaceous escarpments are well known from many regions of the world, since they are typically rich in rudists aragonite fragments determining high percentages of porosity. In these respect the deep knowledge on the facies architecture of these depositional systems is of broad interest as can offer examples for the prediction of the geometry and distribution of the facies types. Subsurface studies based on seismic data require comparisons with analogues from outcrops that allow the observation of structure and sedimentary characters of the MTDs.

On this topic, we carried out a sedimentological study in northwestern Sicily on a well-exposed Cretaceous escarpment, (Custonaci Cretaceous Escarpment, CCE). At present the original escarpment is dismembered in several tectonic units in the Maghrebian Chain. The biostratigraphic data allow to constrain the beginning of the slope sedimentation at the lowermost Cretaceous. Along the succession, the MTDs formed by huge bodies of megabreccias, alternate to finer grained skeletal rudstone and floatstone emplaced by turbidity currents and grain flows. The presence of pillow basalt intercalations suggests a major role of the tectonics as trigger for the MTDs emplacement. Furthermore, synsedimentary listric faults, slump scars and channel filling megabreccias allow to reconstruct the present day polarity of the slope.

The emplacement of coarse megabreccia beds at Custonaci can be documented until the Santonian. However, upward alternances of Scaglia-type pelagic calcilutites and skeletal turbidites and debrite beds lasted up to the Maastrichtian.

Nevertheless the Tertiary deformations have obscured the relationships of the CCE with the original source areas, there is a tight correlation between the evolution of the Cretaceous Panormide Platform and the studied slope.

# The contribution of outcrop analogues to the characterization of drowned shelf margins: examples from the Biscay-Cantabrian basin (Spain) and the Tertiary Piedmont Basin (Italy)

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Keywords: Outcrop analogue, Drowned shelf margin.

This work highlights the value of outcrop analogues in hydrocarbon exploration and production. Submarine erosional surfaces in shallow water, shelfal and slope settings are examined to explore their potential for producing stratigraphic or mixed traps, seismically tracing the outcrops into their buried counterparts or converting them into synthetic seismic volumes. This enables the identification of new plays and the assessment of relevant reservoir architectures. Attention is focused on erosional surfaces developed along hinged margins undergoing increasing rates of tectonic accommodation, resulting in the development of regional unconformities generated by the tilting and destabilization of oversteepened shelves.

These unconformities develop in actively deforming basins experiencing rapidly increasing and laterally changing subsidence rates. As opposed to the classical sequence boundaries driven by relative sea-level falls, these hinged-margin unconformities result from the drowning of shallow marine systems abruptly onlapped by deeper-water facies, and pass laterally into paraconformities associated to stratigraphic lacunae of regional extent, driven by basin reorganization. While the drowning of carbonate platforms normally occurs for ecological reasons, in hinged margins a basinward tilting produces the drowning of clastic shelves and shows angular unconformities instead of the omission surfaces typical drowned carbonate systems. A model-independent and more flexible sequence stratigraphic approach is required, combined with the analysis of the morphostructural reshaping and the associated change in fairways and depositional processes.

The Tertiary Piedmont Basin, developed over the Alps-Apennines Junction in NW-Italy, shows Oligo-Miocene deepening-upward intermontane to intra-slope basins. Tilted deltaic remnants were left by multiple retrogressive slump scars and submarine canyons, providing the seaward delivery of high accommodationhigh supply turbidites sourced from the collapsed and ravined portions of the deltas. Photogrammetric surveys help to highlight the difference between unhinged conventional sequence stratigraphic models and hingedmargin unconformities. The Mesozoic Basque-Cantabrian Basin records the opening of the Bay of Biscay in NW-Spain. An airborne texturized Lidar survey acquired along large coastal cliffs exposing a thick succession deposited from Albian to Cenomanian, shows submarine unconformities developed along faulted margins, locally originating growing salt ridges flanked by deepwater wedges affected by progressive unconformities. The shelf margins underwent increasing hinged accommodation, causing the drowning of carbonate and clastic shelves, unconformably overlain by turbidite systems.

3D synthetic seismic volumes are obtained from digital outcrop models *via* petro-elastic relationships. A seismic inversion process then defines how much of the original features are restituted by seismic modeling and assesses the attributes for different stratigraphic, geometric and litho-fluid constraints. This enables to link directly observed data to analogue subsurface cases using a "facies" concept driver. The synthetic seismics provides an imaging of submarine unconformities and a good match between sedimentary facies and seismic/ impedance facies, bridging the gap between outcropping depositional facies and seismic facies derived by a forward modeling-inversion-classification workflow.

# Temperature effects on acoustic measurements conducted on bitumen-saturated carbonate rocks of the Majella reservoir (Central Italy)

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Keywords: Carbonate reservoir, acoustic properties, temperature effects.

Unconventional oils are emerging as an alternative hydrocarbon reserve since conventional oil is depleting nowadays. A kind of unconventional oil is bitumen, which is characterized by high density, high viscosity and API gravity less than 10° and these physical properties are temperature sensitive. Thus, an accurate knowledge of the petrophysical properties of bitumen rocks as a function of temperature is a useful tool for the characterization of bitumen reservoirs.

In this work, we investigate the temperature effects on the seismic waves velocity in carbonate-bearing rocks of the Majella reservoir. This reservoir represents an interesting analogue for several onshore and offshore oil fields and it can be defined as a natural laboratory to characterize the carbonate reservoir properties.

We have conducted ultrasonic measurements (at the HPHT laboratory of INGV, Rome) of compressional and shear wave velocities on carbonate samples of the Bolognano formation, which show different bitumen content and effective porosity between 10% and 17%. Wave velocities were measured in a range of temperature from 90 to 25°C at ambient pressure conditions. Firstly, we measured the bitumen density by HCl dissolution of the hosting rock, that has resulted to be included between 1.14 and 1.26 gr/cm<sup>3</sup> at ambient temperature. Then, we have calculated bitumen content of our samples, spanning from 3% (low HC-bearing sample) to 15% (high HC-bearing sample).

In general, our preliminary laboratory data show that P-wave velocities decrease linearly with increasing temperature and the same trend has been observed for S-wave velocities. Within the investigated temperature range, the highest HC-bearing sample shows small velocity variations, spanning from 4.49 to 4.25 km/s for Vp and from 2.28 to 2.17 km/s for Vs. Consequently, the Vp/Vs ratio (about 1.96) is temperature independent, due to the P- and S-waves similar trend with temperature change. Vp and Vs are also influenced by different bitumen level saturation. Indeed, for the same porosity, wave velocities of low HC-bearing samples are generally higher than those of samples richer in hydrocarbon. Furthermore, the samples with the highest bitumen content show a larger gradient of velocities change in the temperature range of about 70-50 °C, within which bitumen is in a fluid state. Conversely, below about 50 °C the velocity gradient is lower because, at this temperature, bitumen changes its phase in a solid state.

In conclusion, our results highlight a temperature dependence for HC-bearing carbonate samples and, according to the literature, they are less temperature sensitive respect to the bitumen sands, suggesting that the high stiffness of carbonate frame can inhibit the bitumen effect. Such petrophysical characterization would provide a better link between seismic parameters and the hydrocarbon properties; this is necessary to employ the seismic method for reservoir characterization as well as for production monitoring.

# Fracture attribute characterization in outcrop analogues by a combined field and multiscale photogrammetry approach: insights from platform carbonates folded in the Pag anticline, External Dinarides of Croatia

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Keywords: External Dinarides, Outcrop analogues, Digital Outcrop Model (DOM).

Field analogues allow detailed studies of fracture networks to improve fracture pattern predictions in reservoirs. Quantitative studies on outcrop analogues, for understanding the relationships between the origin of fractures and their geometrical attributes and spatial distributions, are fundamental for obtain scaling laws as a function of mechanical stratigraphy and the evolution of folding and/or faulting mechanisms.

In this contribution, we describe the preliminary results of a structural study carried out in the Pag anticline, a 30 km-long fold that is well exposed in the homonymous island, in the External Dinarides (Croatia). The Pag anticline represents a good field analogue for folded and faulted tight platform carbonates where integrating field-based structural and stratigraphic analysis, microstructural and petrographic observations, and digitalmapping techniques on Digital Outcrop Model (DOMs) based on "close-range" photogrammetry, to obtain large and robust datasets of fracture attributes. The Pag anticline involves about 1 km of Cenomanian to Senonian layered rudist-bearing platform carbonates, overlain by about 250 m of Early-Eocene Foraminiferal limestones and by a Middle-Eocene foreland succession consisting of 300 m of Dalmatian Flysch. In cross section, the anticline shows an asymmetrical box-type geometry, with high angle to overturned limbs and a wide flat crestal zone. The fold is dissected by major backthrusts and forethrusts, and by two compartmentalized main sets of strike-slip faults, striking N-S and E-W, respectively. Along-strike fold shape, deformation style, and deformation patterns, show a distinct variability that can be explained by a progressive differential fold tightening offset by cross-fold strike-slip fault systems. At meso- to micro-scale, the deformation pattern consists of a complex array of veins and stylolites that formed before, during, and after folding and faulting. Petrographic and microstructural analyses helped to unravel the relative timing of different deformational stages and to reconstruct the fracturing history. To characterize the fracture network at multiple scales, we integrated field surveys with satellite imagery and DOMs reconstructed from drone to ground-based photogrammetry. DOMs were used to obtain 3D fracture network and to create virtual bedding-parallel and bedding-perpendicular planar sections. Field and virtual linear scanline and scan area have been carried out in different tectonic domains of the anticline. A hierarchical organization of fractures is observed, including (1) hectometre-scale fracture corridors crosscutting the whole folded succession, (2) through-going fractures cutting several mudstone beds, (3) strata-bound fractures and (4) a pervasive network of fractures shorter than bed thickness. Our preliminary results suggest that this multidisciplinary approach combining field and lab data with multiscale photogrammetry provides reliable results to better understanding the structural framework and fold evolution, and can effectively increase the statistical strength of field-based fracture quantification studies.

# 3D-modelling of lateral facies heterogeneity of a Chattian carbonate ramp (Salento, southern Italy)

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Keywords: 3D facies modeling, facies heterogeneity, geological reliability.

The aim of this work is to reproduce a three-dimensional metre-scale facies heterogeneity model of the Porto Badisco Calcarenite carbonate ramp (upper Oligocene) that crops out in the Salento Peninsula (southern Italy). Capturing metre-scale facies heterogeneity in three-dimensional models for shallow-water carbonate systems is still controversial due to the possibility of facies coexistence and because their association can change through time and space.

Within this context, the continuous and well-exposed upper Oligocene Porto Badisco Calcarenite carbonate ramp permits detailed study of the lithofacies association' distribution and their architecture along the dip direction depositional profile. Lithofacies association and depositional model of the Porto Badisco Calcarenite are referred to those defined by Pomar et al. (2014), that describe the Porto Badisco Calcarenite as a homoclinal carbonate ramp with a euphotic inner setting characterised by the extensive seagrass meadows, passing basinward into a large rotaliid packstone and coral mounds developed in mesophotic conditions. The more distal part of the oligophotic zone is characterised by rhodolithic floatstone to rudstone and large lepidocyclinid packstone. The outer ramp is characterised by a fine calcarenite. The methodology used in this work combines classical field data collection and 3D stochastic modeling by using Petrel<sup>TM</sup>. All the field data were georeferenced and puts into the software to build the digital outcrop model. The 3D facies model has been obtained after several simulations using two stochastic algorithms (SISim, TGSim), comparing the models reproduce by the two algorithms, matching the depositional geometries and the lithofacies association observed in the outcrop. The 3D modeling is a useful tool to better understand the facies architecture and their complex heterogeneity to better characterise semi-quantitatively sedimentological features for subsurface reservoir studies.

# **Session S14**

# Integrated studies of recent and active deformations onland and offshore

Conveners and Chairpersons Massimiliano Barchi (Università di Perugia) Pierfrancesco Burrato (INGV, Roma 1) Luigi Ferranti (Università di Napoli-Federico II) Fabrizio Pepe (Università di Palermo) Marco Sacchi (IAMC-CNR, Napoli)

#### Seismological analysis along the Taormina Fault (Eastern Sicily, Italy)

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Keywords: offshore Eastern Sicily, Taormina Fault, seismotectonic.

Offshore eastern Sicily is among the most seismically active regions of Italy. The historical Italian earthquake catalogue, reports that some of the last millennium's most destructive earthquakes were located along the southernmost part of the Calabro-Peloritan Arc (1908, Mw=7.2; 1932, Mw = 5.1) and in South-eastern Sicily (1169, Mw=6.6; 1542, Mw=6.6; 1693, Mw=7.4; 1990, Mw = 5.7).

We performed a seismological and kinematic study on the Taormina Fault (TF), a tectonic structure that border the Ionian coast offshore area from the Mts Peloritani. The TF extends parallel to the eastern coast of Sicily from the south of Messina to the south of Taormina, and it is suggested to be the source of strong paleoseismic events.

In order to characterize the seismic activity associated to this structural line, earthquake locations and focal mechanisms were computed. We collected about 200 earthquakes recorded in the period 2000, January - 2017, April by the local seismic network managed by the Istituto Nazionale di Geofisica e Vulcanologia (INGV). These earthquakes occurred in the offshore area surrounding the TF and were preliminary located using a 1D crustal velocity model proposed for the volcanic area of Mt. Etna. Hypocenters are mainly located at depth between 1 and 35 km. In the considered period, the study area was affected by a seismicity with a low-to-moderate energy release: local magnitude ( $M_1$ ) of earthquakes ranges between 1.0 and 3.8.

Earthquake location is performed through the integration of arrival times of local events recorded by the National Seismic Network (NSC), managed by INGV and the NEMO-SN1 seafloor observatory. The NSC consists in more than 150 broadband seismic stations deployed in the area of Sicily, Calabria, Aeolian Islands, and Mt. Etna. NEMO-SN1 was deployed about 25 km offshore from the eastern coast of Sicily, at a depth of 2100 m, in the two periods 2002, October - 2003 February and 2012 June - 2013 June.

We picked the P- and S- phases of the events of our dataset during the deployment of NEMO-SN1 and repicked P- and S- phases of earthquakes having magnitude <sup>3</sup> 2.0. For the other local events, we collected the available arrival times of earthquakes from the INGV catalogs and bulletins.

A joint database has been created, collecting data recorded by both land and marine seismic stations. Therefore, we used a new 1D crustal velocity model, specifically calculated for the Western Ionian Sea from the inversion of seismological data recorded by NEMO-SN1, to locate our dataset. Then, the integrated locations have been performed, allowing the improvement of the earthquake hypocentral parameters. Moreover, we computed the fault plane solutions of 50 earthquakes having  $M_L \ge 2.0$ , to highlight the prevalent kinematic of the TF.

Although our results are preliminary, they will allow us to improve the seismotectonic knowledge of this important active seismogenic structure.

# Geo-referencing techniques of 3d models (SfM): Case study of mud volcano, Village Santa Barbara, Caltanissetta (Sicily)

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Keywords: Geo-referencing, SfM, Deformation.

In the last 2 years we have performed a topographic and geodetic monitoring on an active mud volcano located in central Sicily (Caltanissetta, Terra Pelata locality). The target was to understand how the volcano is evolving morphologically and kinematically. Topographic and geodetic surveys were performed periodically (every 3 months) by using a suite of double-frequency GNSS receivers that where been set-up to monitor the kinematics and to geo-reference cartographic products (DTM, DSM and orthophotos). Digital maps were realized through photogrammetry technics and 3D surface modelling by adopting Structure for Motion (SfM) algorithm (James et al. 2017). Following the aim, morphological variations due to active tectonics and/ or ground movements which deform the area were achieved. The monitoring network has been deployed following a twofold target. The first one, is to observe the deformation and kinematics of the area surrounding the mud volcano. To do this, we fixed a stable benchmark by building a GNSS base and surveys were hence performed with a static D-GNSS. This configuration allows us to obtain a sub-centimetre precision in the point location. Other six points were also built and connected to the base. The second was to georeferencing, with high-precision, a series of ground control point (from now on GCPs) to positioning 3D surface model.

In order to geo-reference the 3D models the receivers were configured as follow:

- RTK mode in the first four surveys;
- In the fifth, Static Ultra Rapid mode;
- In the sixth, we tested the precision of geo-referencing by comparing RTK data with Static Ultra Rapid.
- In the seventh, we coupled TST (Theodolite Total Station) and GNSS (RTK).
- All these techniques highlight the follow results:
- by using RTK mode derived coordinates, show errors of 0.05 m:
- by using Static Ultra Rapid mode, error in data fitting in in the order of one decimetre;
- by using TST coupled with GNSS, the error in data fitting are below 0.03 m.

Models were georeferenced according to all applied techniques, while quality of method was tested during the monitoring period to improve model's generation and their positioning.

Our data show that the combination of TST with GNSS provides a greater precision in geo-referencing digital maps even if it requires a long acquisition time. The results, coming from the monitoring, allow us to quantify volumetric and altimetry changes of the mud volcano which are in the order of  $\pm 1$  dm during inflection or deflection phases. Our data suggest that the surface of mud volcano is experiencing a general trend of uplift in the order of one decimetre.

The methods applied in this work to improve the positioning of objects in remote sensing techniques such as rock clusters, landslides, active structures, coastal morphology (Fonstad et al., 2013).

Fonstad, M.A., Dietrich, J.T., Courville, B.C., Jensen, J.L. & Carbonneau, P.E. (2013): Topographic structure from motion: a new development in photogrammetric measurement. Earth Surface Processes and Landforms, 38(4), 421-430.

#### Geodetic and photogrammetric survey of mud volcano in Santa Barbara village (Caltanissetta): implication of active tectonics

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Keywords: Mud Volcano, Geodesy, Monitoring.

The Santa Barbara mud volcano field is located in central Sicily, along the accretionary wedge forming the Sicilian-Maghrebian fold-and-thrust belt. It is constituted by Neogene-Early Pleistocene deposits that were progressively shortened and displaced during the late Miocene to Pleistocene.

The "Maccalube" of Santa Barbara focus of attention after the paroxysm event occurred in August 2008, (Madonia et al. 2011). The paroxysm was preceded by an intense ground fracturing, with displacement spanning from few centimetres up to one meter, which involved many residential building.

With the aim of understand what trigger paroxysm event (crustal and/or superficial stress field, overpressure of fluids) and to set up a valid geological model able to reduce the geological risk of the urban area, a multidisciplinary study was performed. Workflow has included studies on active (morphometry) and ground deformation, (IGM 95 geodetic benchmark) seismic profiles, and epicentres of earthquakes occurred in central Sicily. Since October 2016, we started monitoring the evolution of Santa Barbara active mud volcano through the installation of a GNSS network along the borders of the area covered by the materials ejected during the paroxysm of 2008 Geodetic measurements were also accompanied by photogrammetric surveys through an Unmanned Aerial Vehicle (UAV) to monitoring the most dangerous area. Photogrammetric data and GNSS measuring were acquired during seven measurement campaigns (October 2016 - April 2018) and after compared each other to achieve information about ground motion and get the best 3D model of the mud volcano.

The GNSS results show as expected that the mud volcano is affected by a radial movement in the order of one centimetre. Moreover, the outcome of photogrammetric surveys showed a more important vertical deformation in the vent area characterized by one order of magnitude more than the GNSS data. In particular, we observe a constant upward movement in the central and northern sector of the vent area, that has been interpreted as a first and fast inflection phase, followed by a slower phase of inflection.

This study can contribute to evaluate if mud volcano activity along the Sicilian-Maghrebian fold-and-thrust belt (e.g. Aragona, S. Barbara and S. Biagio) are just related to independent overpressure fluids phenomena and/or by NNW-SSE compressive regional stress field (Bonini, 2012).

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Madonia, P., Grassa, F., Cangemi, M. & Musumeci, C. (2011): Geomorphological and Geochemical Characterization of the 11 August 2008 Mud Volcano Eruption at S. Barbara Village (Sicily, Italy) and Its Possible Relationship with Seismic Activity. Natural Hazards and Earth System Science, 11(5), 1545-1557. doi:10.5194/nhess-11-1545-2011.

#### Combined luminescence and U-Th dating of Holocene faults in NW Sardinia (Italy)

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Keywords: neo-tectonics, MIS5e, W Mediterranean.

Precise dating of paleo-seismological records is crucial to quantify the frequency and distribution of earthquakes, particularly in regions characterized by low rates of tectonic loading and sluggish seismicity with typical recurrence times of  $10^2$  to  $10^4$  yrs. In this contribution, we have applied luminescence and U-Th series dating to document late-Pleistocene extensional deformation in NW Sardinia. The main faults offset marine terraces correlated to MIS5e (pIRIR<sub>290</sub>  $136 \pm 8$  ka) and MIS7 (pIRIR<sub>290</sub>  $230 \pm 8$  ka), providing a lower bound for tectonic activity. Fault scarps and coeval tensional fractures are systematically sealed by travertine. At the intersection between the master fault and conjugate structures, large travertine mounds accumulated in a coastal wind-dominated system. This provide the opportunity to apply both U-Th series and luminescence dating to constrain the latest age of fault motion. Travertine deposits associated to the main NNE fault were dated and luminescence performed on quartz and k/feldspar grains provided reliable, almost undistinguishable within errors, ages of  $3.3 \pm 0.2$  ka (SAR-OSL) and  $3.7 \pm 0.5$  ka (IRSL<sub>50</sub>). On the other hand uncorrected U-Th ages yield about  $32.9 \pm 6$  and  $31.5 \pm 3$  ka. However, these should be taken as maximum ages cause of high noise related to the abundance of detrital <sup>232</sup>Th. In spite of this discrepancy, the results demonstrate that Sardinia records a previously unrecognized late-Pleistocene to Holocene tectonic activity.

#### The structural architecture of the reactivated Rennick Geodynamic Belt (Northern Victoria Land, East Antarctica)

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Keywords: lineament domanis, Rennick Geodynamic Belt, Antarctica.

The Rennick Geodynamic Belt (RGB) is a regionally-sized deformation corridor separating the tectonic units of the Northern Victoria Land (NVL) and of the East Antarctic craton (EAC). It develops along the onland propagation of the Tasman Fracture Zone of the Southern Ocean between Australia and East Antarctica. The RGB is characterized by a length exceeding 100 km and consists of regional fault strands, including the Rennick Fault. Previous studies revealed that this deformation corridor was characterized by poly-phased tectonic movements since Cambro-Ordovician times (Capponi et al., 1999; Federico et al. 2010). The brittle deformation architecture associated to these fault zones, the sharp-asymmetric subglacial morphology, and the geophysical signature at the Rennick Glacier, as well as the geodetic investigations in NVL, strongly suggest that the region is involved in Cenozoic tectonic activity.

In this work we present the results of a multi-scalar study aimed to highlight the Meso-Cenozoic tectonic evolution/reactivation of the RGB. The analysis is based on a twofold approach that includes inversion of fault-slip data and lineament domain analysis.

The identification of the paleostress field(s) responsible for brittle deformation associated to the main Rennick Faults and the adjacent fault strands is based on the fault and fracture inversion performed through an original methodology based on the multiple Montecarlo approach. Results from the different inversion approaches are also discussed.

The lineament detection from synthetic scaled images (MODIS mosaic of Antarctica) of the landscape (including both the ice sheet surface and the outcropping mountains) is performed with automatic procedures (Cianfarra and Salvini, 2014; Cianfarra and Salvini, 2015; Lucianetti et al, 2017). Domain identification follows a two-step processing: *i*. after the polynomial Gaussian fit by grid analysis, the association of the found Gaussian peaks of adjacent analyses allows to identify the Gaussian domains; *ii*. lineaments are then classified/ associated to the corresponding Gaussian domain. In this way we infer the most recent tectonic pathway and the associated crustal stress field.

The integration of the two approaches allows to highlight the polyphased kinematic history and relative ages of the RGB and to better understand the geodynamic setting of the boundary between the EAC and the NVL.

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#### Capo Granitola-Sciacca Fault Zone (Sicilian Channel, Central Mediterranean): Structure vs magmatism

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Keywords: Sicilian Channel, lithospheric fault zone, magmatic manifestations.

The tectonic framework of the northern sector of the Capo Granitola-Sciacca Fault Zone (CGSFZ), a NNEoriented lithospheric strike-slip fault zone located in the Sicilian Channel (southern Italy), has been reconstructed with the aim to define its geometry, kinematics and tectonic evolution and clarify the relationships between the fault zone and the magmatism observed in the area. A large dataset composed of multichannel seismic profiles, Chirp profiles, magnetic and borehole data was used. A set of analogue models has been carried in order to constrain the tectonic processes that led to the observed structural setting. This study has allowed to recognize several magmatic manifestations (volcanic cones, buried magma ascents and sills) in addition to the edifices known in the Graham and Terribile banks.

The CGSFZ is bounded by the Capo Granitola Fault System (CGFS) to the west and the Sciacca Fault System (SFS) to the east, dominated by positive flower structures generated by inversion of NNE-oriented late Miocene normal faults. Only the southern part of the CGFS consists of a sub-vertical, N-S oriented strikeslip master fault. The sector between the fault systems does not show a Plio-Quaternary tectonic deformation, except for the Terribile Bank that is affected by WNW to NW-trending normal faults developed during late Miocene and later reactivated. This set of faults is active at the Terribile Bank, whereas is buried by Plio-Quaternary deposits in the central-northern part of the CGSFZ. The analogue models highlighted a right-lateral movement (Fedorik et al., 2018) that is in contrast with the present-day left-lateral motion showed by GPS data and focal mechanisms. We speculate that the CGSFS developed during a lower to mid-Pliocene tectonic stage, in a right-lateral strike-slip tectonic regime. Afterwards, a new tectonic phase, inducing a left-lateral strike-slip tectonics, occurred since late Pliocene, as result of the change in the direction of the African plate with respect to the fixed Eurasia, from NW to NE (Mantovani et al., 2014). Finally, both the SFS and the CGFS shows evidence of Quaternary tectonics.

The magmatism might be driven by a mechanism of non-plume origin. Magmas rise along the faults of the CGFS and SFS, which cut the lithosphere reaching the asthenosphere and producing partial melting by simple pressure release. Most of the magmatism develops along the strike-slip master fault associated with the CGFS and the normal faults of the Terribile Bank. The magmatic feeding of this bank would be related to lateral magma migration coming from the SFS. In the central-northern part of the CGSFZ, magmas migrate upward along lithospheric faults, then move laterally and rise through NNE and NW-trending buried normal faults. These faults may have favoured the emplacement of sills, which in turn may explain the observed volcanic centres.

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#### In search of the seismogenetic fault of the March 23rd 2018 earthquake (Mw 3.7) near Brindisi (Apulia, Southern Italy): Quaternary structural setting of the southeast Murge Adriatic offshore

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Keywords: Murge Adriatic offshore, Quaternary, Active fault.

The central part of the Apulian foreland, including Murge area (Apulia region) and its Adriatic offshore (southern Italy), have been generally considered practically free from significant level of seismicity. However, historical documentation, seismically-induced soft-sediment deformation structures in Quaternary sediments, and some instrumental observations suggest that the activity of local minor tectonic structures could have been "masked" (and partly also induced) by that of major seismogenic structures located in the neighbouring Appennines and Dinarides-Hellenides orogens. An additional support to this conjecture derives from the recent March 23rd 2018 earthquake, occurred in the southeast Murge Adriatic offshore, for wich INGV estimated a moment magnitude Mw 3.7 (http://cnt.rm.ingv.it/event/18504011). This was the strongest shock recorded in central Apulia since a regional instrumental network, managed by the Bari University Seismological Observatory, has monitored the local seismicity, starting from 1980.

The fault plane solution calculated by the INGV has mainly the character of a strike-slip mechanism with an extensional component, defining two possible fault striking, one about North-South and the other East-West, dipping toward West or South, respectively (<u>http://cnt.rm.ingv.it/event/18504011</u>). In order to explore the possibility of identifying the seismogenetic fault, the present study investigates the effects of faults activities on the Quaternary seismostratigraphic unit of the southeast Murge Adriatic offshore, namely around the epicenter. For this purpose, public unmigrated seismic profiles and exploration wells logs, available in the ViDEPI Project (<u>http://unmig.sviluppoeconomico.gov.it/videpi/videpi.asp</u>) have been used. The interpretation of the seismic lines, up to about 2 km in depth, allowed us to recognize a southward dipping fault kinematically characterized by an extensional component, and displacing the Quaternary seismostratigraphic unit; the fault, that is located few kilometers North of the epicenter, has been traced for a length of about 40 km.

Regional literature research studies revealed that the structural style of the Southern Adriatic area is characterized by re-activated Mesozoic crustal-scale faults. Therefore, according to the plunge, a deep geometric reconstruction of the fault detected in the present research study has been attempted up to 25-30 km, i.e. the depth of the focus of the earthquake (<u>http://cnt.rm.ingv.it/event/18504011</u>). This geometric reconstruction shows that the focus approximately lies on the fault plane, which, in addition to the consistency with the focal mechanism, makes plausible the association of the March 23rd 2018 earthquake to the activity of this fault.

## Active deformation between the Campania Plain and the Apennines based on integration of geological, geomorphological and seismological data

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Keywords: Seismotectonics, Campanian Plains, Southern Apennines.

The Campania region encompasses two different tectonic domains of recent and active deformation. The Tyrrhenian margin, to the west, is a subsiding sector showing ~N-S trending Quaternary extension, a low-rate historical and instrumental seismicity and the interplay between volcanic and tectonic processes. In contrast, NE-SW trending Middle Pleistocene-current extension and high-rate seismicity dominates the uplifting mountain chain to the east.

To investigate the structural interaction between these sectors, and how active and seismogenic deformation is expressed in each of them, we started a multidisciplinary study integrating seismological and geologicalstructural data. We focused on a NE-SW trending regional transect spanning the submerged shelf, the Campania Plain, the western margin and the axis of the northern Campanian Apennines.

In the Apennines, the last 30 years seismicity has been prevalently characterized by isolated event with M<3.5 and by the occurrence of low energy seismic sequences and swarms ( $M_L < 5.0$ ) with hypocentres generally within the first 15 km of the crust. With the exception of the local seismicity of Vesuvio and Campi Flegrei volcanic areas, characterized by single and/or swarm-type activity of low energy (M<2.5), the background seismicity in the Campanian plain showed temporally and spatially isolated events with magnitudes of less than 3.0. Seismicity concentrates close to the Massico mountain ridge, in the north-western sector of the plain, and along the Avella mountain ridge. Offshore, isolated events occur (M max 3.7) at a depth not exceeding 13 km.

Preliminary relocation of the background seismicity that occurred in the last 4 years in the study area shows that seismic activity in the Campanian Plain, with the exception of those related to the volcanic areas, is virtually lacking. The few seismicity localizes along the eastern border of the plain on the first outcrop of the Apennine Chain. Few low magnitude events ( $M_L < 2.5$ ), localized along the WNW-ESE lineament of the Avella Ridge, show kinematics that seem compatible with transtensional motion.

Preliminary work on the exposed faults along the flank of the Apennines has shown a complex structural transition between the uplifting and subsiding areas, where the NW-SE striking faults are segmented by E-W striking faults, which control development of local, relatively deep local basins. Structural analysis revealed the existence of two sets of differently oriented slip lineations on the major faults, which we relate to two different kinematic regimes. A first set trends ~NNW-SSE and is associated to left-transtensional slip on the E-W striking faults.Instead, a second set trends ~NE-SW and is associated to normal to right-transtensional slip on the same faults. The NE-SW extension axis recorded by faults is in agreement with large (e. g. 1980 Irpinia) and moderate (e. g. 2013 Matese) earthquakes occurred in the chain.

#### Geophysical features of shallow crust in Sicily from well log data

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Keywords: Sonic log, P-wave velocity, density.

Many deep wells drilled in Sicily by oil companies, although not homogeneously distributed, are available and contribute to estimate reliable petrophysical parameters of the shallow crust in different geodynamic contexts. We have selected about 30 deep wells, mainly located along the Gela foredeep - Hyblean foreland system and surroundings, and analysed sonic log data in comparison to the stratigraphic profiles. The borehole sonic instrument contains one or more transmitters that emit high-frequency acoustic waves travelling through the formation to two or more receivers that record full waveforms. The difference in the arrival times of the sonic wave trains recorded by the detectors is used to determine the sonic velocity. Sonic log data have been used to better characterize in situ P-wave velocities in the shallow crust and to build a velocity model for the upper 5-6 km. A detailed crustal velocity model is fundamental for different purposes especially in tectonically complex regions. Indeed, from wave velocities, retrieved from sonic "slowness", we have inferred rock density values for homogeneous intervals, following an empirical relationship between sonic velocity and density in sedimentary rocks. These direct data can contribute to build a robust 3D model of the area, together with other geological and geophysical information inferred independently. In Sicily the present-day stress field orientations (IPSI 1.1 database, Mariucci and Montone 2018) delineate a complex tectonic picture evidencing adjacent areas characterized by distinct stress regimes: in the northern offshore of Sicily and in the Hyblean plateau the alignment of horizontal stress is consistent with the crustal motions, whereas different directions are observed along the belt and foredeep. In particular along the northern offshore of Sicily, several earthquakes, with prevalent reverse focal mechanisms, describe a clear ~NNW-SSE current compression. In southeastern Sicily, breakout data along the Hyblean foreland are all consistent with ENE-oriented minimum horizontal stress. Moving to the Gela foredeep, the minimum horizontal stress rotates spatially from ENE-WSW to NW-SE. Along the northern Sicilian belt, a diffuse area with N-S-extension has been recently well depicted; nearby the Tindari-Letojanni fault, the direction abruptly changes into WNW-ESE extension. In the offshore of eastern Sicily up to eastern Calabria, a strike-slip regime with NE-SW-oriented minimum horizontal stress is well defined.

Mariucci, M.T. & Montone, P. (2018): IPSI 1.1, Database of Italian Present-day Stress Indicators. Istituto Nazionale di Geofisica e Vulcanologia (INGV), <u>http://doi.org/10.6092/INGV.IT-IPSI.1.1</u>.

#### Tectonics of the southwestern Sicily offshore based on multi-scale analysis of seismic reflection profiles

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Keywords: Tectonic setting, active tectonics, southwestern Sicily offshore.

The tectono-sedimentary evolution of the NW Sicily Channel has been related to a lithospheric transfer zone made up of two transcurrent fault systems, Capo Granitola (CGFS) and Sciacca (SFS), whose activity pulsed during the Pliocene-Pleistocene (Argnani et al., 1986; Antonelli et al., 1988; Argnani, 1993; Fedorik et al., 2018). No clear evidence of present-day tectonic activity along the CGFS and the northern part of the SFS is nowadays reported (Fedorik et al., 2018).

The joint analysis of ministerial and industrial multi-channel and unpublished single-channel seismic reflection profiles supported by well-log data allowed to make a detailed reconstruction of the morpho-tectonic evolution of the southwestern Sicily offshore.

Off Capo Granitola, we traced a  $\sim$ 4 km long escarpment (Capo Granitola escarpment, CGE) which represents the forelimb of a regional fold (Mazara Fold) submerged west of the study area in a sector where no structures were mapped so far, and two anticline folds (CGF1 and CGF2), which deform an  $\sim$ 3 km wide area, cored by pre-Quaternary seismic unit. The folds represent the shallower and active expression of the northern part of the CGFS.

Offshore Sciacca, we mapped a ~16 km long NNE-SSW trending anticline flexure (SF) related to a flower structure. Growth wedges of stratigraphically-correlated reflectors show that the SF grow at least until the Middle-Late Pleistocene, and associated faults cut Holocene reflectors.

Also, by comparing the NW Sicily Channel and the on-land area struck by the 1968 Belice earthquake, we suggest that the Castelvetrano-Campobello di Mazara escarpment (Barreca et al., 2014) and the CGE belong to a segmented, active tectonic belt which corresponds to the thrust front of the Sicilian orogen.

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## Geological, seismological and geodetic evidence of active tectonics south of Mt. Etna (eastern Sicily)

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Keywords: Eastern Sicily, Ionian offshore, active deformation.

Geological studies and morphological analysis, compared with seismological and geodetic data, suggest that south of the Mt. Etna volcano (eastern Sicily) distinct tectonic processes have acted contemporaneously, i.e., shallow thrusting and folding at the front of the Sicilian-Maghrebian thrust belt and extensional faulting along the Ionian sector. In particular, a large WSW-ENE trending anticline, interpreted as detachment fold, is growing west and north of Catania city (the Catania anticline, De Guidi et al., 2015). Geological data suggest that during the last 6000 years the frontal fold has been characterized by uplift rates of  $\sim 6$  mm/yr along the hinge, consistent with the interferometric data (10 mm/yr) recorded in the last 20 years. Moreover, a NNW-SSE oriented axis of compression has been obtained by seismological data, consistent with GPS measurements over the last 20 years which have revealed a shortening rate of  $\sim 5$  mm/yr along the same direction. High resolution seismic-reflection data show that contractional structures extends in the south-eastern offshore of Mt. Etna where syn-tectonic deposition into a "piggy-back" basin setting (growth folding) is also observed (Barreca et al., 2018). Asymmetric folding appears to deform the post LGM deposits as well as the seafloor, and it has been related to thrust migration. North-eastwards, in the continental slope of the Ionian Sea, a belt of normal faults (the seaward extension of the transtensional Timpe fault system) dislocate the Lower-Middle Pleistocene Etnean clayey substratum and younger deposits, producing ruptures in the seafloor. Besides the activity related to the volcanic feeding system, the seismotectonic pattern of this area can be certainly framed into the regional geodynamic processes. Thrusting and folding can be related to the late migration of the Sicilian chain front, accommodating the compressive regime currently occurring northwards at crustal depth, whereas oblique faulting to the east is probably part of a major tectonic boundary located in eastern Sicily (Gutscher et al., 2015).

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#### The present-day GNSS velocity and strain rate pattern of Italy

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Keywords: GNSS, strain-rate, Italy.

I present an up-to-date high resolution picture of the ongoing crustal deformation field of Italy, based on an extensive combination of continuous and episodic GNSS observations carried out since 1994. The analyzed dataset includes i) more than 1200 continuous GNSS sites available at INGV (<u>http://ring.gm.ingv.it;</u> INGV RING Working Group, 2016), ASI (<u>http://geodaf.mt.asi.it</u>), Netgeo (<u>http://www.netgeo.it</u>), Italpos (<u>http://it.smartnet-eu.com</u>), EUREF (<u>http://www.epncb.oma.be</u>) and from various networks developed on Italy and surrounding regions by local institutions and agencies mainly for mapping, engineering and cadastral purposes, ii) more than 150 episodic GNSS stations, mainly located in Sicily, in Northern Apennines and in Albania. Raw GNSS observations have been processed by using the GAMIT/GLOBK software packages. To adequately study the crustal deformation field over the investigated area, the estimated GNSS velocities have been referred to a fixed Eurasian reference frame. In addition, by taking into account the observed horizontal velocity field and associated uncertainties, we computed the 2D strain-rate tensor over the investigated area. Because of the heterogeneous spatial distribution of our velocity field data, in interpolating the velocity field, I adopted a uniform Gaussian weighting function. Such approach allowed me to obtain a finer resolution over the entire investigated area.

INGV RING Working Group (2016): Rete integrata Nazionale GPS, doi:10.13127/RING.

#### Morphometric analysis of the north-western Sicily sector and its implications for the neotectonics

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Keywords: Morphometry, Stream network, Morphotectonic.

Quantitative analysis of landscape is a powerful tool to study both vertical and horizontal topographic response to recent tectonic forcing. Vertical perturbation of base level can be deciphered by integrated analisys of the spatio-temporal distribution of both river incisions and depositional systems, while horizontal shift of trunk streams and pattern of river terraces can be used to infer horizontal tectonic perturbation. A morphometric analisys was performed in an area located between Palermo and Termini Imerese (north-western Sicily) characterized by sectors with flat topography and intervening ridges. The drainage network is composed by six hydrographic basins, namely from W to E: Oreto, Eleuterio, Milicia, San Leonardo, Torto and Imera Settentrionale, whose trunk streams are oriented from NE-SW to N-S. Different indexes were obtained from the quantitative analysis of a high resolution digital elevation model, which were subsequently integrated and validated with field data and remotely sensed image analysis. Horizontal shifting of the drainage networks, which was inferred by mean of the determination of their transverse topographic symmetry, highlights that the river networks are horizontally deflected towards two topographic lows located between the Eleuterio and Milicia drainage basins, and between the San Leonardo and Torto drainage basins, respectively. Specifically, the Oreto and Eleuterio rivers are deflected about 1 and 3 km, respectively, towards the SE while the Milicia river is deflected about 4 km toward W. The Imera Settentrionale and Torto rivers are shifted about 1.5 and 4 km, respectively to WSW, while San Leonardo river is shifted about 3 km to SE. Such deflections are also confirmed by unpaired fluvial terraces detected in the areas where the fluvial deflection is inferred. The integrated analysis of the positions of knick-points along the trunk streams, which are not related to lithological variations, and multiple hypsometric (e.g. catchment, trunk stream and stream network) allows the detection of the erosional imprint due to tectonic forcing for each studied hydrographic basin. The bi-modal statistical distribution of the catchment elevation classes related to the Oreto, Eleuterio, Torto and Imera Settentrionale drainage basins show their transitional state while, on the contrary, the Milicia and San Leonardo drainage basins are not responding to a recent vertical perturbation. The data we present improve the understanding of the Northern Sicily response to the recent tectonic activity.

## Evidence for quaternary tectonic activity from the reconstruction of the buried quaternary bottom surface in the North-Eastern corner of the Friuli plain (NE Italy)

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Keywords: North-eastern Italy, geophysics and geognostic, Quaternary tectonic activity.

This study deals with the reconstruction of the buried north-easternmost sector of the Friuli plain, through the analysis of seismic and wells subsurface data. The interest was focused on the most recent stratigraphical horizon, here interpreted as the bottom of the Quaternary succession, with the aim to detect the Quaternary activity of the main faults.

The eastern Friuli-western Slovenia area is characterized by the interaction of two different deformational systems: in the western sector prevails thrust activity, in the eastern one dominates strike slip tectonics. Main fault-systems show an about E-W trending in the W-sector and a NW-SE trending in the eastern one. Both deformational systems are subjected to NNW-SSE compressional regime (Serpelloni et al, 2016), responsible of their reverse or transcurrent/transpressive kinematics. Their activity is testified by the recent and historical seismicity of the area (Mw6.63, 1348; Mw6.32, 1511; Mw6.45, 1976) (Rovida et al, 2016), but their seismogenic role is still not completely clear. In this contest, Quaternary activity has been assumed for the Susans Tricesimo thrust (Poli & Zanferrari, 2017), while recent paleoseismological investigations revealed Quaternary dislocations on the Colle Villano thrust (Falcucci et al, 2018).

In this study industrial seismic lines interpretation, together with deep well logs data, allowed to reconstruct the geometry of the main stratigraphical horizons (from the top Cretaceous-Paleogenic carbonatic platform to the Quaternary base) and the main tectonic structures of the buried eastern Friuli plain. In particular, through the implementation of well logs data it was possible to reconstruct the thickness of the buried alluvial Quaternary deposits and to identify the tectonic influence on the bottom of the Quaternary surface. By merging these new data with morphotectonic and field observations, the main buried active faults of the area were detected and possible estimates of their activity rates were performed.

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## Geomorphic response to the late Quaternary tectonic deformation along the eastern margin of the Hyblean Plateau (SE-Sicily, Italy): the case study of the Avola Fault

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Keywords: SE Sicily, Avola Fault, Morphometric analysis.

Establishing the activity of single fault segments, within a regional-scale fault belt, is one of the hardest challenges for the risk assessment of a region. Although in the last decades, geomorphic analyses have been widely applied in detecting active tectonics, unravelling debated tectonic issues, the occurrence of a fault, its geometry, kinematics and slip-rates, often are based on the qualitative analysis of its morphotectonic features (e.g. topographic scarps, valleys shape, offset geomorphic/geological markers).

The present study focuses on the morphometric analysis of the eastern border of the Hyblean Plateau (SE Sicily, Italy) that represents the topographic expression of the foreland bulge of the Sicily collision belt. The eastern margin of the Hyblean Plateau is controlled by a 40 km long NE oriented fault belt, including the right-stepping Ispica-Pozzallo and Avola normal fault segments, that experienced a Quaternary polyphase tectonic evolution. The Ispica-Pozzallo Fault shows evident morphologic and kinematic signatures of its recent remobilisation, whereas the activity along the Avola Fault is mainly suggested by the deformation of the marine terraces and by the geometry of the drainage system dissecting the footwall of the structure.

The present study aims at defining the age of the landscape geomorphic responses along the Avola Fault, in order to test the seismogenic potential of the structure. This study achieves this goal by carrying out fluvial network and relief analyses, including the investigations of river terracing. In particular, based on detailed Digital Elevation Model (DEM), we apply different geomorphic indices, such as hypsometric integral (HI), topographic relief (TR) and dissection (TD), stream length (SL) index,  $k_{sn}$ , Vf, combined with long-profile investigation, along-stream knickpoints modelling, semi-quantitative geomorphological analyses, a field-based geomorphological survey and meso-scale structural investigation. We mainly find that the Avola Fault extends for about 20km and actually consists of two distinct fault segments. The analysis of the geomorphic features along the fault highlights that the landscape not adjusted yet and is still reacting to the tectonic processes. Furthermore, the differential geomorphic responses along the fault, higher in the central sector and decreasing towards the tips, is consistent with a recent half-elliptical deformation at the footwall of the Avola Fault. Our results confirm previous interpretation, predicting the growth of the Avola Fault in the last 300 ka, with an estimated vertical slip-rates ranging from 0.6 mm/a to 1.15 mm/a.

## Active volcano-tectonic deformations: a 3D seismic reflection experiment in the resurgent dome of the NYT Caldera (Pozzuoli Bay, Campi Flegrei, Naples)

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Keywords: 3D seismic cube, volcano-tectonic deformations, NYT Caldera.

An ultra-resolution, 3D seismic reflection data cube was collected during an oceanographic cruise organized in the frame of a joint project involving Italian research institutions, the University of Palermo, Catania and Napoli, CNR of Napoli and INGV Roma, and two companies, the Geo Marine Survey System (The Netherlands) and GeoSurvey (Portugal). The data acquisition approach charted during this cooperation was based on innovative technologies for the offshore imaging of stratigraphy and structures at continental margins with horizontal and vertical resolution at decimetric scale. In this work, we present the methodology used for the 3D HR-seismic reflection data acquisition and the preliminary interpretation of the 3D seismic cube. The 3D seismic data were acquired onboard the N/O Minerva Uno by using an innovative data acquisition equipment composed by two sparker sources fired in flip-flop mode, and eight HR 48-channel, slant streamers, with group spacing variable from 1 to 2 meters, at 10 kHz sampling rate. An innovative navigation system was used to perform all necessary computations to determining real-time positions of sources and receivers. The investigated area is located in the central-northern part of the Pozzuoli (Naples) Bay that represents the offshore prolongation of the Campi Flegrei caldera. Here, an antiformal structure, corresponding to the resurgent dome associated with Neapolitan Yellow Tuff (NYT) caldera, characterizes the structure and morphology of the inner shelf (e.g. Sacchi et al., 2014). Previous research works based on 2 or 2.5D high-resolution reflection seismics (e.g. Steinmann et al., 2018), have documented the presence of collapse faults on the summit (apical graben) of the resurgent dome. However the 3D pattern of this structure and the style of ground deformation are still poorly defined. The results of this study provide the base for the quantitative analysis of active faults and stress field that are important for understanding the volcano-tectonic process responsible for the formation of the resurgence dome inside the caldera and its related hazard.

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#### An evaluation of the seismic/geodetic deformation in the Sicily Channel (Italy)

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Keywords: Sicily Channel, seismic-geodetic deformation, seismic catalog.

The Sicily Channel has been affected by extensional tectonic processes, since Late Miocene and mostly during the Pliocene which leaded to the development of a number of tectonic depressions (e.g. Pantelleria, Linosa and Malta troughs). These tectonic depressions have been interpreted as large and discrete pull-apart basins involving deep crustal levels that developed in front of the Africa-Eurasia collisional belt within a large dextral wrench zone The Sicily Channel is a region with a potentially moderate seismic and volcanic hazard, due to the occurrence, in the recent past, of volcanic eruptions sometimes accompanied by significant seismic swarms (Mmax  $\leq$  5).

In order to provide an improved picture of the seismic characteristics of the Sicily Channel, we compiled a seismic catalog by taking into account all information coming from available instrumental catalogues reports and instrumental data recorded covering the period 1981-2017. Moreover, taking advantage of the availability of a set of continuous GNSS stations installed along the southern Sicilian on-shore, we propose an improved picture of the current crustal deformation pattern over the investigated area. To this aim, we collected and analyzed all available data coming from the permanent GNSS stations installed across the Sicily Channel as well as the southern Sicilian onshore, spanning the 1999-2018 time interval. In addition, based on our GNSS and seismological observations, we provide a preliminary evaluation of the seismic/geodetic deformation-rate ratio for the investigated area.

## Seismotectonics of Ancona Adriatic offshore: an attempt to construct a 3D velocity model for relocating earthquakes on the Ancona-Rimini coast

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Keywords: Earthquakes, 3D velocity model, NonLinLoc.

The Northern Apennine foredeep, between Rimini and Porto Sant' Elpidio reaches thicknesses of more than 4 km of Plio-Pleistocene terrigenous sediment. These later, overlie the Meso-Cenozoic Umbria-Marche stratigraphic succession outcropping in the structures of the mountain belt. The foredeep overlaps the western medium Adriatic region, characterized by historical and instrumental seismicity with potentially high magnitude.

The thin-skinned structural style of the arcuate foreland fold-and-thrust belt dissects the foredeep in different sectors, in a complex structural setting where the focal depth of seismic events is poorly constrained, especially using one-dimensional velocity models. Moreover, seismographs network geometry with azimuthal gap greater than 180° reduces the constrain of locations..

A 3D velocity model calibrated for the area, permits to get accurate locations and error reduction, especially on focal depth.

A catalogue containing only the onshore/offshore earthquakes (registrations  $\geq$  5) occurred from December 1996 to December 2015 along a coastal strip between Rimini and Porto Sant' Elpidio, has been considered.

The Umbria-Marche crustal and mantle setting is well highlighted by a tomographic model proposed by Carannante et al. (2013). This model is not properly constrained for the Adriatic offshore due to the scarcity of events and for the external position of this area respect the centre of the tomography grid. Localise earthquakes using this model, produces in fact associated errors even higher than those obtained using a 1D velocity model.

To overcome these limitations, a 3D model has been developed integrating geophysical and geological data, derived both from collected data along the coast and from the industrial geophysical survey. The produced 3D model has been integrated with the seismic tomography model and used for relocating with the nonlinear location algorithm of NonLinLoc.

Nevertheless, although there are lower associated errors than the 1D and 3D-tomography-derived locations, the proposed mixed 3D model could be improved.

To improve the results, the best NonLinLoc location has been used to relocate with the double differences algorithm (HypoDD). This software is less dependent on the velocity model and permits location errors reduction.

In the Mt. Conero area, the earthquake's relocation permits to define the crustal portion involved in the deformation. For the Ancona area, an onshore/offshore geological cross section has been drawn, integrating structure's geometry and the deformation style derived from the reinterpreted seismic reflection profiles, calibrated with the thickness and lithology of the industrial wells to reach a seismotectonic interpretation for the region.

Carannante, S., Monachesi, G., Cattaneo, M., Amato, A. & Chiarabba, C. (2013): Deep structure and tectonics of northerncentral Apennines as seen by regional scale tomography and 3D located earthquakes. J. Geophys. Res., in press, 118, 1-13.

## An example of Late Quaternary negative tectonic inversion along the Sibillini Thrust Front (central Apennines): the contribution of an integrated geological and geophysical investigation

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Keywords: central Apennines, Sibillini Thrust Front, negative tectonic inversion.

We discuss the results of an integrated geological and geophysical study carried out in the the Arquata del Tronto territory, epicentral area of the August 24th 2016 Mw 6 earthquake (central Apennines), in order to test the existence of a potentially active fault segment in the surroundings of the Pretare and Piedilama hamlets. In this area, the pelitic-arenaceous succession of the Messinian Laga Formation form a pair of N10 oriented overturned E-verging folds, representing the ramp anticline and the footwall syncline of a splay of the major Sibillini Thrust Front. The continuity of the paired folds is interrupted along a discrete N10 oriented alignment, marked by an impressive 5 km-long sharp west facing scarp, modelled on very erodible terrains, that locally dam the drainage system, dissecting the eastern slope of the Sibillini Mountains. Along this morphological feature, we performed a 1:5000 scale field mapping, supported by the interpretation of borehole data and integrated with the analysis of aerial photos and satellite images. The geological and geomorphological investigations were combined with 75 environmental noise measurements, processed through Horizontal to Vertical Spectra Ratio technique (HVSR), 4 Multichannel Spectral Analysis of Surface Waves (MASW), 3 Refraction Microtremor (REMI) tests and 1 seismic refraction tomography (SRT).

The collected data provided the constraints to reconstruct 1:2000 scale detailed geological sections across the investigated feature. The results of our investigation point out the occurrence of a N10 oriented west-dipping normal fault, deriving from the negative tectonic inversion of the previous splay of the Mt. Sibillini Thrust Front. Our data evidence that the fault segment was active during the Late Quaternary and affected debris-flow deposits as young as 125 ka. These are vertically offset for about 50 m, constraining a minimum vertical displacement-rate of 0.4 mm/a.

In conclusion, our study illustrates an example of Late Quaternary negative tectonic inversion along the trend of the Sibillini Thrust Front, different from the dominant NW-SE oriented seismogenic normal fault systems, responsible for the main seismicity of the region.

#### Active tectonics in the southern Matese area: insights from geomorphological, morphometrical, stratigraphical, structural and tephrostratigraphical data

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Keywords: active tectonics, Matese massif, southern Apennines.

The Matese massif is a NW-SE trending carbonate ridge, 40 km long and 20 km large, located in the northern sector of the southern Apennines chain. It is bounded, to the NE and to the SW, by the Bojano and Alife intramontane basins respectively. The latter are fault-controlled continental basins, filled with several hundred meters thick successions of continental deposits interbedded with tephra layers. Alluvial fan system grew at the toe of the Matese ridge, along both the Alife and Bojano areas. The SE sector of the Matese massif, which did not record historical moderate to strong seismic events, has been struck on the 29<sup>th</sup> December 2013 by a 5.16 Mw earthquake that caused diffuse ground effects (Valente et al., 2018). The 2013 event led to a large interest about active tectonics along the southern slope of the Matese ridge, which is bounded by the Alife basin. We have carried out a multidisciplinary study on active tectonics in this sector of the Matese massif. The study has been based on the integration of geomorphological analysis of detail scale topographic maps (Technical Map in scale 1:5,000 of the Regione Campania), GIS-aided morphometrical analysis of 5m DTM, stratigraphical, structural and tephrostratigraphical analysis of outcropping Quaternary deposits. Our data show that evidence of recent faulting are widespread in the southern Matese area, particularly along the socalled South Matese fault zone (Ascione et al., 2018). This evidence includes offset late Quaternary deposits and tectonics controlled geomorphological features, such as fault scarps formed in Quaternary deposits, river bends, wind gaps, water gaps, etc. Morphometrical analysis of alluvial fans located at the toe of the Matese ridge suggest tectonic subsidence in the area between the villages of Raviscanina and Piedimonte Matese (RPf) faster with respect of the San Potito Sannitico area (SPf). Slope/area analysis of river network dissecting the southern Matese ridge point to the occurrence of a focus of enhanced convex long profiles along the RPf. Overall data suggest active faulting along the South Matese fault zone and the adjoining Alife basin, with a local increase of tectonic subsidence along the RPf area, as it is testified by morphometrical analysis of the topography and of the river network.

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- Valente, E., Ascione, A., Ciotoli, G., Cozzolino, M., Porfido, S. & Sciarra, A. (2018): Do moderate magnitude earthquakes generate seismically induced ground effects? The case study of the Mw = 5.16, 29th December 2013. Matese earthquake (southern Apennines, Italy). International Journal of Earth Science, 107(2), 517-537.

### **Session S15**

## Tectonic and geodynamic control on large earthquakes and complex earthquake sequences: case studies from Italy and not only

Conveners AND CHAIRPERSONS Giuseppina Lavecchia (Università "G. D'Annunzio" Chieti-Pescara) Giancarlo Neri (Università di Messina) Roberto Scarpa (Università di Salerno) Riccardo Caputo (Università di Ferrara)

#### 3D geological reconstruction of the Nera River basin (Central Italy): relationships between seismogenic faults and groundwater circulation

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Keywords: Seismogenic faults, 3D model, Carbonate acquifer.

The 2016-2017 seismic sequence of the Central Italy caused the reactivation of a complex NNW-SSE trending, WSW-dipping normal fault system associated with important co-seismic ruptures. The seismic sequence significantly affected the groundwater circulation hosted in limestone aquifers. The main effects can be summarized in spring discharge variation (both positive and negative), water-table rises and river discharge increases, especially in the upper part of the Nera River basin.

In this work we study the relationships between the complex structural setting and the water circulation, in order to understand how the reactivation of the seismogenic faults has influenced the hydrological system of the upper basin of the Nera River. The relationships between the faults and the main aquifers have been analyzed through a 3D geological model down to a depth of 2 km and comprising the area extending from Ussita and Castelsantangelo sul Nera to Mts. Sibillini thrust.

The construction of the geological model was firstly based on a revision of the existing cartography of the area. Subsequently, using the geological map of the Sibillini Mountains (Pierantoni et al., 2013), we have created a grid of 10 geological sections. In order to create the 3D model, all the geological maps and the sections were elaborated using the software Move Midland 2017. The model comprises the main structural elements, such as Sibillini thrust and the seismogenic faults reactivated by the seismic sequence (i.e. M. Bove-Vettore fault system), and the main hydrogeological elements, top Maiolica formation and top Corniola formation surfaces, representing the top of the main aquifers. Particularly important is the top of Corniola formation, considering that it represents the top of the basal aquifer, composed by Corniola and Calcare Massiccio formations. Finally, we report the distribution of seismic events and related co-seismic ruptures separated in the different time sequences.

This model allows us to understand the geometrical relationship between the main aquifers and the crosscutting seismogenic faults. Together with the hydrogeological data, this model contributes in the understanding of the medium-long term evolution of the hydrological system of the upper Nera River basin.

Pierantoni, P., Deiana, G., & Galdenzi, S. (2013): Stratigraphic and structural features of the Sibillini mountains (Umbria-Marche Apennines, Italy). Italian Journal of Geosciences, 132(3), 497-520.

#### Geological/seismological data for the generation of a 3D fault model: the southeastern Sicily 1693 earthquake case study

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Keywords: 1693 earthquakes, macroseismic intensities, Sicily seismicity.

Our study focuses on the area of maximum damage of the 1693 main shocks (9 and 11 January, Mw $\approx$ 6.1 and Mw $\approx$ 7.3, respectively). Numerous secondary effects (liquefaction, landslides, fractures and ruptures), described by historical accounts, caused important landscape modifications in the eastern side of the Hyblean Plateau. However, given the absence of clear evidence of surface faulting and relevant faults in the area of maximum effects, several faults located nearby were associated to these earthquakes (see DISS Working Group, 2015 and references therein).

We performed a revision of the macroseismic data of the 1693 shocks and mapped in detail the seismogeological effects. The most numerous and relevant effects occurred in the sector embracing Palazzolo, Lentini and Catania, suggesting that the sources of the 1693 earthquakes are located in this area. The 11 January earthquake is located northward, probably offshore, due to the following tsunami generation..

To observe the recent activity of faults crossing the area, we performed: a detailed fault mapping, through DTM and aerial photos analyses and geological-structural surveys; a geomorphologic analysis and the morphometric study of four rivers flowing in the area. We mapped NE-SW and NW-SE faults and a NNE-SSW major fault system (PBFS), running for about 30 km, from Palazzolo up to Brucoli and probably extending offshore. Geomorphological and morphometric analyses highlight recent tectonic activity associated to some of the mapped faults, with specific reference to the NE-SW system and PBFS.

To constrain the geometry and kinematics of the detected faults, we analyzed instrumental seismicity: about 1500 earthquakes with  $0.4 \le M \le 4.6$ , recorded during 1994-2017 by the Istituto Nazionale di Geofisica e Vulcanologia. Shocks are mainly characterized by strike slip or transtensive mechanisms (Musumeci et al., 2014) and a low-to-moderate energy release at depth 10-25 km. Most of the earthquakes are located offshore in the Ionian Sea between Catania and Siracusa, on land in the Augusta area, in the Palazzolo - Canicattini area and across the Avanfossa Gela-Catania. Seismicity distribution depicts two main clusters along a N-S direction overlapping the area affected by most seismogeological effects and nearby the NNE-SSW PBSF is mapped.

A 3D fault model of the likely structures involved in the sequence is constrained by an integrated structuralkinematic-seismological approach.

DISS Working Group (2015): Database of Individual Seismogenic Sources (DISS), Version 3.2.0: A compilation of potential sources for earthquakes larger than M 5.5 in Italy and surrounding areas. <u>http://diss.rm.ingv.it/diss/</u>, INGV: DOI:10.6092/INGV.IT-DISS3.2.0.

Musumeci, C., Scarfi, L., Palano, M. & Patanè, D. (2014): Foreland segmentation along an active convergent margin: new constraints in southeastern Sicily (Italy) from seismic and geodetic observations. Tectonophysics: <u>http://dx.doi.org/10.1016/j.tecto.2014.05.017</u>.

#### Subsurface geology and seismogenic faults in the area struck by the 2016-2017 earthquake sequence (Central Italy): a seismic reflection study

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Keywords: Earthquakes, Seismic Reflection Profiles, Central Italy.

This work is aimed to provide a reconstruction of the subsurface geology of the region struck by the longlasting 2016-2017 Central Italy seismic sequence, which activated a ~60 km long, complex system of NNW-SSE trending normal faults. Co-seismic surface ruptures were observed to mostly reactivate well-known, longterm Quaternary faults. At depth, the geometry and kinematics of the activated faults were constrained by earthquakes location and focal mechanisms, as well as by combined modelling of strong motion and geodetic measurements.

In order to fill the gap between shallow and deep observations, we interpreted a large data-set, consisting of 4 deep boreholes and 97 2-D seismic reflection profiles, both stack and time-migrated, most of which previously unpublished and kindly provided by ENI S.p.A.

The results are here synthetized along three ~50 km long, WSW-ENE trending representative geological sections, interpreted down to a depth of 12 km, crossing the regions affected by three mainshocks occurred in 2016, whose epicenters were located (North to South) in the areas of Visso (26th October, Mw= 5.9), Norcia (30th October, Mw=6.5) and Accumoli (24th August, Mw=6.0), respectively.

Along these sections, the style of deformation of the compressional fold-and-thrust belt is characterized by superposed, multiple detachments, where the uppermost portion of the acoustic basement is involved only in the major thrust sheets. The stacked tectonic units, consisting of carbonates and turbidites, are cut and displaced by WSW-dipping (and antithetic ENE-dipping) normal faults, characterized by listric geometry, dipping 60° to 70° at the surface and gradually decreasing their dip at depth.

Comparing the reconstructed subsurface structure with the earthquake distribution, we observe that the seismicity is confined within the sedimentary sequence and does not penetrate the acoustic basement, whose top, constrained at depths of 8 to 11 km, strongly controls the lower seismicity cut-off. At shallower depths, seismicity is rarely observed within the turbiditic Laga succession, at the footwall of the Sibillini thrust. Summarizing, our reconstruction provides a coherent image of the subsurface setting of both compressional and extensional structure, and of the seismogenic faults in particular, compatible with the observed seismicity distribution.

Our results can help in understanding the seismic phenomena in terms of rheology of the involved rocks and interaction between the activated segments. Next step of our work will be to complete a 3-D reconstruction of the activated fault system, a goal that necessarily call for productive and open-mind interactions with specialists of other research groups and institutions.

#### Field and geophysical clues for the prosecution towards the SE of the Aeolian-Tindari-Letojanni Fault System (NE Sicily-southern Italy)

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Keywords: Aeolian-Tindari-Letojanni Fault System, active tectonics, seismicity.

The Aeolian-Tindari-Letojanni Fault System (ATLFS) in southern Italy is a major NNW-SSE trending belt of tectonic structures that extends from the central sector of the Aeolian Arc to the mainland of NE Sicily across the Peloritani mountains. As suggested by earthquakes clustering in the area, most of the fault strands forming the ATLFS are still seismically active with seismic events (about 1800 in the last 30 years) that mainly localize on its northern sector. As a whole, a number of works concerning seismological, geodetic and geological data strongly contributed to constrain the structural style and the current kinematics of this sector of ATLFS. On the contrary, despite the ATLFS can be geologically detected on field as far as the Ionian coast, the southern branch remains poorly studied and hence it seismic potential not fully understood. Recently mapped faults and seismicity in the Ionian Sea, suggest a possible prosecution of the ATLFS also in this sector. However, connection between on-land and offshore tectonic structures hasn't been attempted so far.

In this preliminary contribute we aimed to investigate this possible connection by means a multidisciplinary approach which has included field and marine geology, earthquakes location and seismic tomography. Geostructural data were collected from Rocca Novara locality (NW) to the Capo S. Alessio promontory (SE) and suggest right-lateral strike-slip kinematics on NW-SE trending fault planes. In the near-offshore, singlechannel seismic line clearly display that the continental shelf is down faulted and the younger sediments in the hanging-wall seem to fanning up towards the fault where ascent of muddy material also occurs.

Earthquakes distribution and computed focal solutions revealed that in the offshore, the southern segment of the ATLFS splits into two branches with distinct kinematics. Transpression occurs on the southern one which consists of a SW-dipping, NW-SE striking tectonic structure deepening up to 15 km of depth. Multichannel seismic profiles clearly evidenced contraction at shallow crust level alongside this earthquakes alignment. Conversely, oblique extensional kinematics characterize the northern branch which consists of a major NE-dipping, NW-SE trending tectonic structure. The latter can be traced on the seismic tomography since it appears to dislocate the Moho located in the area at about 35 km of depth. Although the on-land fault segments show no evidence for recent activity, since they deform rocks not younger then the Miocene, kinematics on fault planes is consistent with current stress field evidenced by computed focal solutions.

This may suggest that on-land fault segments (20 km-long) may have been reactivated under the modern stress field and could be prone to release earthquakes with considerable magnitude also considering historical (i.e. the 1780 seismic sequence) seismicity and that a seismic gap seems to occurs between Rocca Novara and Capo. S. Alessio.

#### 3D fault model of the Campania-Lucania (southern Italy) 1980 earthquake from new field evidences and seismological data

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Keywords: Campania-Lucania 1980 Earthquake, Structural Geology, 3D Seismotectonic Model.

At the light of new geological data integrated with revised seismological data, a detailed and original 3D seismotectonic fault-model of the Campania-Lucania (southern Italy) 1980 earthquake ( $M_w$  6.9) is built. Structural field work was carried over a large area (~2400 Km<sup>2</sup>) along the traces of the Quaternary extensional fault system outcropping within the 1980 earthquakes epicentral area. Long-term and co-seismic fault/slip data were acquired by digital survey using FieldMove application.

Three major fault alignments, each one articulated in segments and sections, with characterizing attitude, rake and offset, were identified and stored in a GIS database. The inner and intermediate alignments, e.g. Inner Irpinia (InIF) and Irpinia Faults (IF), dip eastward; the outer alignment, e.g. Lucania Fault (LF), is antithetic with respect to IF. Both the InIF and the IF strike in an average NW-SE direction along the northern and central segments and rotate in direction WNW-ESE/W-E along the southern segments.

After nearly 40 years since the 1980 earthquake, relevant co-seismic fault scarps with vertical displacement up to  $\sim$ 1 meter are still well evident. They outcrop prevailingly along the IF trace, for a total discontinuous length of  $\sim$ 35 km, and subordinately along the InIF and the LF.

A detailed 3D geometric fault-model, extrapolated to the base of the seismogenic layer, was built with the Move Midland Valley software by integrating the georeferenced fault traces with their section-view trace geometry. The latter was derived from serial seismological sections across the hypocentral area (1980 aftershock data relocated by Scarpa et al. in this conference and ISNet seismic events 2005-2011 M<sub>L</sub> $\leq$ 3, from De Matteis et al., 2012), from interpretative geological cross-sections and from a geologic reinterpretation of the CROP 04 profile. A corresponding 3D kinematic model was obtained by stress inversion of fault-slip data and focal mechanisms.

The reconstructed 3D earthquake/fault association highlighted that the time-space evolution of the 1980 multi-event earthquake was controlled by an interconnected fault system consisting of the InIF, the IF and LF. The first rupture, at the origin time, propagated from north to south along the NE-dipping IF segments; the second rupture, at 20° sec, activated the N-to-NNE-dipping southern segment of the InIF and/or of the IF; the third rupture, at 40° sec, developed along the antithetic LF. The possible seismogenic role attributed to the southern InIF segment represents one of the novel results of our interpretation and may have strong implication in terms of seismic hazard evaluation.

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## Paleoseismic slip of the Mt. Vettore fault revealed by detailed morphologic survey of the bedrock fault scarp (2016 central Italy earthquakes, M 6.5)

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Keywords: 2016 central Italy earthquake, normal faulting, coseismic slip.

The August-October 2016 central Italy earthquakes, which had a maximum magnitude of Mw 6.5 during the October 30 shock, reactivated the Mt. Vettore - Mt. Bove normal fault system in the Sibillini Mts. The earthquakes produced primary coseismic surface faulting along the entire ~30 km-long fault system (Civico et al., 2018). Spectacular evidence of surface faulting with nearly dip-slip net displacement up to 2.4 m was produced in the central part of the Mt. Vettore normal fault. With the purpose of studying the Mt. Vettore bedrock fault scarp, a detailed morphologic field survey was carried out by terrestrial LiDAR and terrestrial photographic surveying. In particular, we surveyed a  $\sim 70$  m-long scarp located in the central part of the Redentore section of the Mt. Vettore normal fault, at an elevation of  $\sim 2100$  m a.s.l., where the 2016 coseismic slip was  $\sim 2$  m. After processing the LiDAR and image acquisitions we obtained a 3D point cloud with average spacing between adjacent points of 4±2 mm. The heights, along-dip lengths and slope angles of the fault scarp were analyzed on the 3D topographic model through graphic procedures along several topographic profiles. We recognized three scarp generations, including the 2016 coseismic scarp. The third scarp (oldest) is much higher than the previous ones, suggesting that it might result from the cumulative displacement of two surface faulting events. Therefore, we recognized 4 surface faulting displacement events. Using the scarp heights measured on the 3D model and correlating the recognized displacement events with paleoearthquakes dated in paleoseismologic trenches and available in the literature (Galli et al., 2017a, 2017b), the slip rate (~1.2 mm/yr) and the slip history diagram for the last few millennia have been reconstructed.

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- Galli, P., Castenetto, S. & Peronace, E. (2017a): The macroseismic intensity distribution of the 30 October 2016 earthquake in central Italy (Mw 6.6): Seismotectonic implications. Tectonics, 36, <u>https://doi.org/10.1002/2017TC004583</u>.
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#### Field image of a foreshock-mainshock pair: the Amatrice (M<sub>w</sub>6.0)-Norcia (M<sub>w</sub>6.5) 2016 earthquakes case (central Italy)

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Keywords: 2016 Central Italy Earthquake, Mt Vettore Fault, Coseismic slip distribution and segmentation.

We analyze the pattern of coseismic surface faulting occurred along the Mt Vettore-Mt Bove fault (VBF, central Italy), repeatedly activated during the 2016 Central Italy seismic sequence climaxed at the 30 October 2016, Norcia mainshock ( $M_w$  6.5).

More than 3800 measurements of coseismic ruptures and 350 fault plane attitude were sampled along the VBF and stored in a comprehensive GIS-managed database reporting, for each survey site, the fracture type, attitude, kinematics (whenever possible), throw and opening.

Subsequent elaborations led us to assess the coseismic surface-rupture length, rupture area, maximum and average throw and displacement and kinematics associated of the main events.

Comparing the data collected along the Vettoretto-Redentore Fault segment (VRS) after the 24 August foreshock ( $M_w 6.0$ ) with those collected after the 30 October mainshock ( $M_w 6.5$ ), we found that throw values associated to the foreshock and the mainshock differ by ~ one order of magnitude (27 cm *versus* 217 cm maximum values). Nevertheless, the slip profiles display a similar multi-scale sinuosity controlled by the long-term fault segmentation pattern at different hierarchical orders. Additional statistical analysis of the fractures allowed us to calculate the percentage distribution of the different types of fractures with respect to the fault segmentation and the dispersion of the different fracture types from the long-term trend.

Along the VRS slip profile, three well distinct wavelength orders of fluctuations are recognized that reflect the long-term hierarchic organization in fault segments, sections and sub-sections. The peaks of coseismic displacement, on fault sections and sub-sections activated by both events, have the same along-strike position.

The 24 August ruptures on the VRS affected mainly two fault sections which exhibit distinctly different amounts of maximum and mean slip. A high slip gradient characterizes the lateral transition between them. The 30 October event, completely activated the VRS segment whose intermediate section, namely the Redentore section, shows the largest displacement and both its northern and southern continuations are characterized by sharp high lateral slip gradient.

The 30 October mainshock also ruptured the northernmost VBF. The overall observed surface slip exhibits a roughly sinusoidal distribution, where wavelength, maximum displacement and mean slip progressively decrease northward.

Finally, we calculated along the VRS, both the geologic and topographic long-term displacement and compared the obtained results with the diagram of coseismic displacement. The offset of the topographic slope across the fault scarp, was measured and interpreted as displacement cumulated by several slip events after the demise of the Last Glacial Maximum (LGM), that is after  $\sim 15\pm3$  kyrs ago. The calculated vertical displacement was used to estimate the post-LGM throw rate.

# The role of advanced tomographic images in unravelling the complex history of tectonic inversions, fault segmentation and large seismic sequences occurrence in the central Apennines (Italy) normal fault system

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Keywords: inherited faults, tectonic inversion, seismic sequence.

Inherited geological structures and crustal heterogeneities play a substantial role in the earthquake generation processes. Even large-scale discontinuities could be remobilized as a consequence of orogeny evolution, especially during tectonic inversions, causing diffuse fault segmentation. Such process strongly contributes in limiting the faults extent, and consequently the earthquakes maximum magnitude. Moreover, it has been generally observed that the overprint of different deformational styles due to tectonic inversions could mask the surface expression of deep structures.

The central Apennines represent an exemplary case for such issues since the alternation in time and space of compressional and extensional stages created the conditions for episodic tectonic inversions. In this context, it is rather difficult to estimate the potential slip deficit still pending on unbroken segments of fault systems, due to the uncertain lateral and vertical continuity of faults and their possible decoupling.

In this contribution, we discuss new evidences given by the analysis of seismicity and advanced velocity tomograms of an 80-km long section of the normal fault system of the Central Apennines (Italy) activated during the 2009 and 2016-2018 seismic sequences.

Inherited compressional structures, still dominating the general style of the Apennines belt architecture, actually interfere with the active extension. Th joint interpretation we present highlight how the extensional seismic sequences partially reactivated previous structures. Such observed complexity, derived from the irregular geometry of normal faults and inverted thrust ramps, is responsible for the intense fragmentation of the current extensional system and the peculiar development of last decades seismic sequences.

The better recognition and tridimensional definition of such faults, their lateral and vertical development and their relationship with recorded seismicity is finally a key issue for seismic hazard assessment.

## Seismological and statistical analyses of 2009 L'Aquila and 2016 Amatrice-Norcia seismic sequences (Northern-Central Italy)

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Keywords: L'Aquila, Norcia, earthquake.

The L'Aquila seismic sequence stroke the central regions of Italy from the beginning of 2009, with a mainshock of moment magnitude Mw 6.1 on 06/04/2009 (epicenter in Roio). The seismicity reached again the typical level of background in approximately 2012. The Amatrice-Norcia seismic sequence has been active since the first major earthquake on 24 August 2016 (located near Amatrice), followed by a mainshock of Mw 6.5 on 30 October 2016 (located near Norcia). The latter sequence interested areas in northern-central Italy which were partially covered by the formerly cited sequence. Seismic activity is still on progress at the time of writing this abstract.

In this work, seismic catalogues were acquired from the Italian Seismological Instrumental and parametric Data-basE (ISIDE) and later from INGV Centro Nazionale Terremoti, for both seismic sequences. The Dobrovolsky equation (Dobrovolsky et al., 1979), where the strain radius of the maximum circular area of precursors scales with the magnitude of the impending strong earthquake, has been used as a spatial criterion to select circular seismic areas to be studied. At the same time, other regions were selected according to the major tectonic structures responsible for the seismic sequences.

Statistical tests were performed, focusing on variations in space and time of the *b*-value from the Gutenberg-Richter Law (Gutenberg & Richter, 1956), since it has been considered a potential seismic precursor for M>5 events in several studies (for example Papadopoulos & Baskoutas, 2009; Papadopoulos et al., 2010). The *b*-in-time diagrams were plotted and sliced into different time windows to evidence variations before and after great shocks during the two sequences; after that, the results were compared. On the other hand, *b*-in-space maps and cross-sections of selected regions were drawn (as in Montuori et al., 2016), in order to follow the 3D evolution of the seismic sequences along the main seismogenic structures.

#### New dating the coseismic deformation of Santa Tecla Fault by Lichenometry method on Mt. Etna volcano (Sicily)

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Keywords: coseismic exhumation, free-face fault plane, lichenometry.

The eastern slope of Mt. Etna t is characterised by shallow seismicity originating from normal-oblique faulting (the Timpe fault system, related to WNW-ESE regional extension. Several interpretations of the unstable eastern flank of Mt. Etna indicate a simple gravity-controlled mechanism enhanced by magmatic intrusions. Conversely some Authors indicate one or more causative factors or interaction between them (regional stress, gravity forces and dike-induced rifting) to produce the slow sliding of eastern flank of the volcano. The reconstruction of the extensional active tectonic structures on the eastern flank of Mt. Etna and of the related earthquakes, allowed De Guidi *et al.* (2012) to calculate that the fault population on Mt. Etna's eastern flank follows a scaling law which magnitude is usually two-orders lower than worldwide fault populations. In particular, the minimum earthquake magnitude to have ground rupture effect is ca. 2.5. This system is characterised by high frequency seismic activity, because the thinned seismogenic layer crust. Thus the earthquakes hypocentral occur between 0.5 and 2 km.

Earthquakes affecting the medium-lower eastern flank has been historically reconstructed by macroseismic analysis and reported in "Macroseismic Database and Etnean Earthquakes Database from 1832 to 1998". In recent decades instrumental seismic registration provide the seismological parameters unable to evaluate focal mechanism, hypocentre and relative algorithms related to geometric parameters which control the growths of fault segments.

In this paper, we present a new methodology to evaluate the age of the coseismic exhumation of free-face fault plane of the NNW-SSE oriented normal fault segment named S. Tecla, belonging to the Acireale-S.Alfio Fault system. It is consist in the measure of the thalli species (Lichenometry method) (Beschel, 1960; Gregory, 1976; Innes, 1981, 1985; Cook-Talbot, 1991; Armstrong & Bradwell, 2009, 2011; Trenbirth, 2010; Bull, 1996, 2003; Joshi 2012) in order to know the parameters characterising their grown. The seismic history of the S. Tecla Fault indicates eight events (1865 - 2001) with  $3,4 \div 4,7$  Magnitude. We found Evidence of recent rapid vertical deformation at the base of the S. Tecla fault scarp characterised by 20 m long and 25 cm high nude surface exposed. We have observed that there are thalli of *Xanthoparmelia conspersa* (Ach.) Hale, they are colonizing part of the nude surface in the escarpment studied. The results highlight that the older detected and analysed thalli was dated about 42 years ago, showing that previous seismic events have generated the surface where the thalli rooted. The displacement of this surface could be related to the seismic events happened on the 2 and 9 March in 1952 (Azzaro's report) in Linera and Rocca d'Api seismic area causing cavities, cracks, ruptures on the ground in length for 6 km.

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#### Characterization of the quality of earthquakes' location in Italy

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Keywords: Seismicity, Earthquake locations, Italian Seismic Network.

The "Istituto Nazionale di Geofisica e Vulcanologia" (INGV) is the authority responsible for the seismic monitoring of Italy since 1981. During the last 30 years, the INGV built a network for the seismic monitoring the whole Italian territory that has been growing both in quantity and in quality of the installed instruments. The network counts today more than 300 seismic stations (mainly broadband) and represents a valuable tools for researches in seismology and related disciplines.

Every four months the official catalogue of the Italian seismicity, the "Bollettino Sismico Italiano" (BSI), is released. The number of earthquake occurring in Italy during a year can be even in the order of some tens of thousands when large sequences occurs; as for instance the Central Italy sequences during 2009 and 2016/17, with main shock Magnitude of 6.3 and 6.5 respectively. Each seismic event is described by its origin time and spatial coordinates which just represent the best estimation for the inverse problem of earthquake localization. Inevitably each localization is affected by errors introduced by the simplified velocity models and the quality of the data.

In this paper we follow three main aims: i) try to summarize the complicated spatial patter of the seismic distribution; ii) mapping the distribution of the earthquake focal parameters and their relative uncertainties; iii) find possible correlation between the data used in earthquake hypocenter estimation and the quality of the locations themselves.

For those purposes we selected from the BSI all the seismic events recorded by the Italian National Seismic Network and published in the BSI with earthquake Magnitude  $\geq 2.5$  occurred from January 2012 to May 2017. The geographical extension ranges from about 6° and 22° of longitude E and from 34° to 48° of latitude N to be more focused on the Italian territory. The whole catalogue lists 3149 events.

This work gives new insights on the capability and on the limitations of the network, and allows a more comprehensive characterization the geological complexity of the Italian territory. Finally, this work points out the weaknesses of the Italian Seismic Network, and represents an useful tool that could address the future development of the network following the objective of a more robust and reliable characterization of earthquakes across the country.

## The RETRACE-3D multi-data and multi-expertise approach towards the construction of a 3D crustal model for the 2016-2018 Central Italy seismic sequence

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Keywords: 3D modeling, seismic sequence, geological maps.

The RETRACE-3D project (centRal italy EarThquakes integRAted Crustal model) has been promoted, with the coordination of the National Department of Civil Protection (DPC), with the ambitious idea to combine together the best data and expertise in order to produce, as first result, a new, robust and of broad consensus, 3D crustal model of the area interested by the 2016-2018 Central Italy seismic sequence.

More than 60 researchers and experts from the Italian National Research Council (CNR, IGAG and IREA), the National Institute of Geophysics and Volcanology (INGV), the Geological Survey of Italy (Department of ISPRA), and the DPC collaborate on the project.

The RETRACE-3D Working Group (<u>www.retrace3d.it/Gruppo.html</u>) benefits from the best available geological, geophysical and satellite datasets deriving from their own institutional activities and kindly provided by ENI and TOTAL companies, in the frame of the National Service of Civil Protection, that includes also private organizations.

All the datasets, with some additional resources (e.g. literature, task reports), are shared through a projectdedicated repository and metadata catalogue (WP0), with restricted user access to confidential data.

The RETRACE-3D project structure includes a first step (WP1) of data preparation, to provide the participants with common harmonized and ready-to-use datasets. They are distinguished as input and comparison datasets, used respectively in WP2-WP3 and WP4.

Further elaboration steps include: i) the construction of a preliminary 3D crustal model (WP2) mainly based on surface geological constraints, seismic reflection profiles and deep boreholes, gravity maps and modeling; ii) the extension of the 3D model to seismogenic depths (WP3) integrating the preliminary model with further information coming from Local Earthquakes Tomography (LET), thermal and rheological data, gravity and magnetic crustal modeling.

The final step (WP4) will be a geometric and kinematic validation (e.g., balancing and analogical modeling) and a cross-check against comparison datasets (e.g., SAR, GPS, coseismic surficial effects, seismogenic sources characteristics, Quaternary geology-geomorphology-neotectonics, seismic catalogues) not used during the modeling phases.

The RETRACE-3D approach has been designed to maximize the information and constraints from multidisciplinary datasets and the benefits deriving from the interaction among a great number of researchers from different disciplines to obtain the most consistent and comprehensive 3D crustal model for the area. This approach, despite time consuming, will overcome the weaknesses that are inherent in more common 2D or 3D not multidisciplinary approach. The final 3D model will serve as a starting point for following geo-mechanical numerical simulations and will be able to give answer to many different geological and seismological problems.

## UNICT\_NET discrete geodetic network: monitoring of aseismic and coseismic ground deformations in different Italian peninsula areas affected by active tectonics

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Keywords: deformation, aseismic, coseismic.

Since 2014, the Earth Science Section of the University of Catania, started a project for the training of a GEOmatica laboratory staff. The main team skills is to analyse the deformation in various scenarios. The applications are: analysis of post critical hydrogeological emergency; seismic events; volcano-tectonic deformation; monitoring with geodetic instruments (GNSS, Total Station, UAV application).

The GEOmatica\_laboratory designed benchmarks of UNICT\_NET in order to satisfy the following criteria of deformation analysis:

- Measurement along ground surfaces affected by active geological processes, through both measure of discrete points (GNSS, total station, and levelling applications) and high-resolution field topography by Structure from Motion (SfM) method (UAV Unmanned Air Vehicles application);
- Starting and allocation of "field 0" along active geological structures (Start-chronology-UNICT\_NET fields);
- Monitoring of areas characterised by a deformation with variable magnitude scale both in space and time
  related to dissimilar rheological behaviour of the substratum.

Therefore, we have identified some areas in italian peninsula, affected by different processes of related to active deformation:

- The deformation bands along the active faults present on Etna volcano;
- Inter-, co- and post-seismic deformations along the fault segments of the Umbria-Marche Apennines;
- Sedimentary volcanism (the maccalube of S. Barbara Caltanissetta, central Sicily).
- Assuming previously conditions, the positioning of network benchmarks follow these criteria:
- The distribution of the existing permanent and discrete benchmarks belonging to different networks that were active before the year 2014 (IGM; RING; CAGEONET; DPC; ISPRA; NETGEO; Etna@ref);
- The seismotectonic and volcanotectonic setting of the areas in relation to seismic data and to reactivated structures;
- Surface and deep geometry of the active structures related to the structural and tectonic setting;
- Morphostructural stability in both static and dynamic conditions at sites where the new benchmarks are built.

Finally, the distribution of the benchmarks was planned in order to reconstruct the principal deformation zone, which developed because of the historical event. Therefore, the network was planned as following:

- Much closer to the deformation source area;
- Equivalent distances from the active structures (eg. fault length area, outcropping of volcanic structures, dykes, inclined sheets, volcanic reservoirs;
- In topographic analysis, within a determined distance from the closest permanent network points not affected by deformation, allowing a rigorous elaboration during the post-processing phases.

To date, the results have provided main information about geometry, kinematic and local stress field, which allowed, together with seismic and geophysical data, to evaluate the criteria of strain and ground ruptures useful to upgrade the information useful to mitigate geological hazards.

## 3D reconstruction of the Mt. Vettore seismogenic fault system: geometric and kinematic relationships with the Sibillini Thrust, Central Apennines (Italy)

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Keywords: 2016-2017 seismic sequence, Central Apennines (Italy), Seismogenic faulting.

The 2016-2017 Amatrice-Norcia seismic sequence was triggered by the reactivation of a complex NNW-SSE trending, WSW-dipping fault system cross-cutting the Umbria-Marche fold and thrust belt. This fault system produced important co-seismic ruptures in the hanging wall of the Sibillini Mts. thrust, whereas less evident or absent ruptures were observed in the footwall. A strong debate exists in the literature about the geometry of the seismogenic faults and its relationships with inherited tectonic structures, such as thrusts or reverse faults developed during the Miocene compressional phase. In this work we propose a novel 3D geological model of the Mt. Vettore area comprised between the Castelluccio basin and the Sibillini Mts. thrust. The model was constructed using a grid of geological sections parallel and orthogonal to the main structural elements (i.e. normal faults and thrusts) down to a depth of 3 km. This model represents the 3D geometry of structural surfaces such as the top of Maiolica formation, the Sibillini thrust and the main seismogenic normal faults. The arrangement of the structural elements evidences the geometrical cross-cutting relationships between the seismogenic normal faults and the Sibillini thrust, indicating that the normal fault system cuts and displaces both the Sibillini thrust and the top Maiolica Fm. surfaces. Through the construction of a set of seriated sections across the Mt. Vettore normal fault system, the vertical cumulative throw distribution and its along-strike variations were also investigated by the interpolated cut-off lines of the reference surfaces. The cumulative geological throw exhibits an important offset that overcomes 1 km in the proximity of the Sibillini thrust southern outcrop, suggesting that the seismogenic fault system continues across the thrust footwall, to the south-east. The cross-cutting relationships between active normal and old compressional structures may be crucial for a better definition of the faults segmentation, and thus of seismic hazard.

## Multiple lines of evidence for a new seismogenic fault north-east of the Mt Vettore Fault (central Italy) - an unexpected outcome of the Norcia 2016-2017 seismic sequence

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Keywords: Active faulting, Norcia 2016-2017 seismic sequence, intra-Apennine extensional domain.

The Norcia 2016, Mw 6.5 earthquake (central Italy) represents one of the most energetic events occurring in Italy in the last 50 years. It is the mainshock of a complex earthquake sequence developed along the ~60 km long, NNW-SSE oriented Mt Vettore-Mt Gorzano (Ve-Go) active normal fault system (Lavecchia et al., 2016). Coseismic deformation has been broadly documented along the main fault scarps for both the 24 August (Mw 6.0) and the 30 October main shocks (Civico et al., 2018 and ref. therein).

The earthquake sequence is mostly attributed to the Ve-Go fault system. Nevertheless, its time-space evolution suggests the activation, starting with the 26 October, Mw 5.9 event of another structure located north-eastward of the Mt Vettore fault. From January to April 2018, several events characterized by normal fault kinematics and Mw $\leq$ 4.6 (http://cnt.rm.ingv.it/en/tdmt) occurred there. Unfortunately, in this sector no clear evidence of active faulting is recognizable in the field, possibly due to the wide outcropping of less resistant rock types (marls and flysch deposits).

In order to collect evidence on the existence of this possible new seismogenic structure, to reconstruct its geometry at depth, and to analyze its role in controlling the earthquake activity, we used multiple lines of evidence including 1) morphometric analysis with DEM-derivatives, 2) structural-geological analysis of the long-term and active deformation, 3) 3D geometric-kinematic analysis of well-relocated available seismological data; and 4) stress inversion of geological and seismological data and fault slip-tendency.

Our results suggest an active normal fault, named Mt Val di Fibbia fault (VFF), which strikes for ~20 km in NNW-SSE direction, dips 55°-65° WSW-ward and is arranged in *en-echelon* geometry with respect to the Ve-Go. Its geometry also ensures a good mechanical tendency to the slip, when considering the overall extensional stress regime, and is coherent with the possible occurrence of Mw $\geq$ 6.0 earthquakes.

The characterization of the VFF, in a sector considered almost aseismic up to date, further highlights the complexity of the central Italy 2016-2017 seismic sequence, revealing itself as a case study suitable in investigating the possible northward extent of the intra-Apennine extensional domain.

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#### Distributed faulting and partitioning of the deformation in normal-faulting events: insights from the October 30, 2016 Central Italy earthquake (Mw 6.5)

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Keywords: Surface faulting, Central Italy earthquake, PFDHA.

Surface faulting is commonly produced by moderate to strong earthquakes (i.e., Mw > 6.0) and is responsible for significant damage. We analyze the database of ground ruptures generated by the October 30, 2016 Central Italy event (Mw 6.5), compiled by the Open Emergeo Working Group (Villani et al., 2018).

We describe both primary and distributed faulting (DF), investigating the factors ruling the distribution of faults and the partitioning of the deformation (Ferrario & Livio, 2018). We found that key parameters are distance from the primary fault, geometry (strike, dip), geology (lithology, mechanical properties of the sediments) but the main factor driving the localization of distributed faulting is the long-term structural array of structures (i.e., presence of antithetic systems, relay zones etc.).

We compute the conditional probability of DF occurrence as a function of distance from the primary fault, using the approach proposed by Youngs et al. (2003) on a dataset composed by the October 30, 2016 earthquake, together with all the events that generated surface faulting in the Italian Apennines since 1980 (i.e., Mw 6.8 Irpinia 1980; Mw 6.0 Colfiorito 1997; Mw 6.3 L'Aquila 2009; Mw 6.0 Amatrice, August 2016).

We found that the currently adopted DF-distance relations, which are based on traditional field surveys, significantly underestimate DF occurrence and do not capture its complex spatial pattern. We argue that the hazard underestimation is related to epistemic uncertainties deriving from an incomplete mapping of subtle DF features, especially in areas far from the main rupture.

We will discuss the implications that failing in the recognition of DF can have on the estimation of key parameters for seismic hazard assessment, such as recurrence intervals, elapsed time and slip per event.

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#### 3D Fault-model building for seismotectonic purposes - Application to Central Italy with some warnings

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Keywords: 3D fault-models, L'Aquila 2009 earthquake, Central Italy 2016-17 earthquake.

Since at least ten years, the building of realistic 3D fault-models with variations along strike and dip has become a standard methodology to constrain earthquake-fault association at depth. Local and regional 3D Quaternary fault-models have been recently built by researchers of the Chieti CRUST-research unit, also in collaboration with elsewhere colleagues. Some of the afforded case studies concerns the intra-Apennine extensional belt of Central Italy and, in particular, the fault systems activated by the l'Aquila 2009 and Central Italy 2016-17 earthquake sequences (Lavecchia et al., 2016 and 2017; Castaldo et al., 2018).

In order to retrieve, in a well-defined geographic reference system, the 3D geometry of the active fault segments involved in the above sequences and neighboring to them, we follow a four step-methodological approach. In particular, we start from a detailed (scale 1:10.000 to 1:50.000) digital map of the fault traces of the individual Late Quaternary normal fault segments and extrapolate them at depth, with different degrees of approximation by exploiting the available geological/seismological information (e.g. geologic and morphotectonic maps, boreholes, cross-sections, fault/slip data, hypocentral datasets, focal mechanisms, available seismic lines).

The 3D fault model is based on the direct interpolation of the available data to build well-constrained fault patches, and on the depth and lateral extrapolation of the patches to form complete surfaces by exploiting the Move 3D Midland Valley software. The geometric uncertainty of modelled fault patch is estimated considering for each fault element two separate factors (completeness of the input data and variability of the geometric attributes).

In the early eighties, John Ramsey was remarking "... Beware of geologist who announces that his sections are perfectly balanced ... He is inexperienced, naive, dishonest or combines these traits".

Also in building 3D fault-models we would always keep in mind these warnings! We must not forget to consider our modelled surfaces as transitionary products that need to be continuously updated, and even abandoned, as new data and constraints arise.

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#### Combined gravity and magnetic anomalies modeling across the area interested by the 2016-2017 seismic sequence in central Italy

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Keywords: 2016-2017 earthquake, central Italy, gravity and magnetic anomaly modeling.

This work presents the results of gravity and magnetic modeling across three WSW-ENE regional sections, crossing the area interested by the 2016-2017 seismic sequence in central Italy. The models have been created using the datasets of the Bouguer anomaly and the magnetic anomaly map of Italy. Modeling of the upper crustal geometries (0-10 km) was constrained to the geologic and structural setting derived from integration of surface observations with an unpublished seismic reflection dataset made available by ENI S.p.a., calibrated by available well logs data. The physical properties of the rock volumes interested by the modeling - i.e. density and magnetic susceptibility - were tested among the ranges proposed in the literature, whilst Curie isotherm depth was constrained with the available heat flow data.

The resulting models provide valid support to the reconstruction of the geological and geophysical understanding of the region, also in terms of an evaluation of the thickness of the seismogenic layer of the area. In particular, the models provide convincing evidences of the control exerted by the mechanical stratigraphy of the upper crust on the thickness of the seismogenic layer, whose base grossly coincides with the top of the basement s.l. The proposed models show a good correspondence between our grav-mag modeling and the results of the interpretation of the seismic reflection data down to ~12 km depth. On a crustal scale, we observe the eastward deepening of the top of the basement and of the Moho discontinuity. Most of the short-wavelength (< 10 km) gravity anomaly signatures occur in the center of the study area, where the mainshocks of the 2016-2017 seismic sequence were registered. The gravity signatures of the Norcia and Castelluccio di Norcia basins are in fact clearly observable and fit by models.

## Surface ruptures geometries and extensional earthquake faults in the Sibillini mountains (Central Italy)

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Keywords: earthquake ruptures, active extensional faults, 2016 Central Italy Earthquakes.

Integration of geological and seismological data remains one of the main objectives when identifying active faults and assessing their potential hazard. A detailed field mapping of spatial geometries of the coseismic surface ruptures is the basis to characterize seismogenic structures and represents an important step toward assessing the recurrence intervals and magnitude of earthquakes. The estimate the likely length and location of future earthquake ruptures on mapped faults remain one of the main tasks in seismotectonics studies. The fault maps can predict where large earthquakes are expected, but deficient about the offset because earthquakes do not always rupture the entirety of the fault on which they occur. When mapped at high details earthquake ruptures, show a propagation from one fault strand to another with a complex array. Structural relations such as fracture length and distributions, fault offsets, shear zone width, links between geometries along the fault strands provide insight into mechanics of earthquake rupture. Moreover, surface ruptures display key structural relationships that are the essential tools for extrapolating and constraining the depth of the fault plane from a kinematic point of view. Several ground ruptures, associated with a significant sequence of earthquakes (Mw 6.1, Mw 6.0 and Mw 6.5) occurred in the Sibillini Mountains in Central Italy in the last quarter of 2016. Over a distance of more than 30 km in the M. Vettore - M. Porche - M. Bove area, different strands of SW dipping extensional master faults and few associated antithetic NE dipping faults has been activated. Detailed structural relationships of the surface ruptures, during the different events, are systematically mapped at scales finer than 1:500 and documented the distribution of all fractures with  $\geq 2$  cm of vertical offset, which totaled more than 5.000 individual scarps. They consist of open cracks and vertical dislocations or warps (2 m maximum throw) striking NW-SE, with multiple overlapping arrangements that can be divided into kinematic sets distributes throughout the width of the pre-existing fault zones. The cross sections highlight slip accommodation through linkage, which shows to be a common fault growth mechanism. The main factors that define the different aspects of rupture zone fabric include: a) the length and architecture of the rupture zone; b) rupture zone thickness; c) kinematics and magnitude of the coseismic slip within the rupture; d) geometric arrangement and relationship of different fracture sets, patterns of splaying, and their degree of interconnectivity. Moreover, the rheology of the ruptures materials (rock, soil, debris), the overburned thickness of the rupture zone width and magnitude of tectonic loading, seems to play an important role in the rupture zone fabric.

#### Seismotectonic analysis of the Matese area (Southern Apennines)

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Keywords: Seismotectonics, seismogenic sources, normal faults.

The Matese area is located at the junction between Central and Southern Apennines. GPS data show NE-SW active extension with velocities across the area > 2 mm/yr. The area is characterized by a high seismicity and several seismic sequences were recorded even in recent times (1997-98 M<4.2, 2001 M<3.6, 2013-14 Ml 4.9, 2016 Mw 4.4). Despite the high extension rates and high seismicity, the active faults are poorly constrained and only two faults have been associated to large earthquakes thanks to paleoseismologic investigations: the Aquae Iuliae Fault (first shock of the 1349 sequence, M 6.8) and the Northern Matese Fault System (208 BC, one shock of the 1456 M 7.2 sequence and 1805 M 6.7 earthquakes) (Galli et al., 2017). In this study, a seismotectonic model of 3D seismogenic sources based on geology, seismicity and geodesy is proposed. The study is articulated in 6 steps: 1) reconstruction of the surficial traces of the main active faults, classified according to their activity; 2) compilation of a database of instrumental earthquakes extracted from the existing seismic catalogues; 3) compilation of geodetic velocity vectors and strain rates from the literature; 4) definition of the thickness of the seismogenic layer by computing an original thermo-mechanical analysis (1D-geotherms and rheologic profiles) and by integrating it with the hypocentral distribution of instrumental seismicity; 5) definition of the geometric, kinematic and energetic parameters of the main seismogenic sources of the Matese area; and 6) assessment and comparison of the geologic, geodetic and seismic strain rates.

We identify 5 main potential seismogenic sources belonging to three NW-SE normal fault systems: 1) a western system composed by the SW-dipping San Pietro Infine and Ailano - Piedimonte Matese + Piedimonte Matese - Gioia Sannitica faults; 2) a central system composed of the SW-dipping Acquae Iuliae - Letino and Gallo - Matese Lake faults; and 3) the NE-dipping Northern Matese Fault System. The Matese Lake fault is poorly constrained.

When comparing the geodetic, seismic and geologic strain rates, a large difference is detected, with geodetic rates much higher than the geologic and seismic ones. Several hypotheses can be advanced, including the possibility that at least two M 6.8 sources, silent since the last 700 yrs, are loading to their expected maximum earthquake, but further investigations are needed.

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### Rupture mechanism of the Campania-Lucania (southern Italy) 1980 earthquake inferred from seismological and geodetic data

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Keywords: Campania-Lucania 1980 Earthquake, Seismology, Seismotectonics.

A detailed reconstruction of the rupture mechanism of the 1980 Campania-Lucania (southern Italy) earthquake is presented. This event is also improperly known as Irpinia earthquake, which is however only a part of the region influenced by macroseismic effects and where the main faults are located. Relocation of the main hypocenters and the estimation of fault-plane solutions of the aftershocks, through P-wave velocity inversion models provide an overall comprehensive picture of the source mechanism. The analysis of available data suggests a complex rupture mechanism, as already identified by many previous studies, which consists of three separate events.

The present work provides however a convincing evidence of almost simultaneous activation of a syntheticantithetic normal fault couple as characterizing rupture source process of this earthquake. The first event activated the northern NW-SE striking segment of a large (~40-km-long), high-angle, NE-dipping, master fault. With the second event the rupture propagated southward along the fault strike and activated the southern WNW-ESE striking segment (~15-km-long) of the same master fault. Conversely, the third rupture occurred along a SW-dipping normal fault antithetic to the master fault northern segment.

This mechanism is well evidenced by the revised location of the hypocenter of the main event, and the location of the aftershocks and their fault-plane solutions, as well as by the underlying three-dimensional P-wave velocity structure. The model originally proposed by Amoruso et al., 2005 that was based purely on the inversion of co-seismic vertical displacement data is confirmed by the present analysis, as it satisfies all of the available experimental observations and better constrains the location and fault-plane solutions of the aftershocks, the velocity discontinuities, and the rupture observations at the surface (see Bello et al. this conference). This conclusion is also supported by analyses of the post-seismic data evidenced by Amoruso et al., 2011.

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#### RETRACE-3D (centRal italy EarThquakes integRAted Crustal model) Project: preliminary results

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Keywords: 3D geological modeling, velocity models, seismogenic faults.

The RETRACE-3D (centRal italy EarThquakes integRAted Crustal model) Project has been launched to build a new 3D geological model of the area struck by the 2016-2018 Central Italy seismic sequence, blending together in a synergic way the multi-disciplinary skills of a large community of researchers and experts of several research institutes (CNR-IGAG, CNR-IREA, INGV, and ISPRA) and National Department of Civil Protection.

The RETRACE-3D Project has been organized in several steps to achieve different goals. The development of a high-quality 3D subsurface structural model will indeed serve as a base for further applications including: i) the possible improvement of velocity models currently used to locate the seismicity and ii) the elaboration of dynamic models of the recognized seismogenic structures.

The study area, more than 5,000 km<sup>2</sup> wide, was investigated for hydrocarbon exploration purposes through the acquisition of a large number of 2D seismic reflection profiles, gravimetric and aeromagnetic data, together with the drilling of some scattered wells. All these existing datasets were kindly made available by ENI and TOTAL companies. Moreover, the RETRACE-3D project dataset also includes geological, geophysical and satellite data deriving from the institutional activities of the involved research institutes.

The preliminary results of the project derive from the integrated interpretation, in the time domain, of 179 seismic reflection profiles, deep borehole data, and surface geological information.

This interpretation step requested a preliminary phase of data preparation where the ample set of data was quality-checked and homogenized to make it ready for further elaborations. As an example, the existing geological data have been harmonized and codified according to a defined regional stratigraphic and structural scheme, while a datum shift has been applied, where required, to the different seismic vintages to refer all the data to the chosen seismic reference datum.

Furthermore, a careful review of the available velocity data, derived from well and seismic data, provided fundamental constraints to elaborate synthetic well logs and a 3D velocity model that will be used to depth-convert the model from the time domain.

The preliminary 3D model is able to shed some light on the structural architecture of the study area. While the extension of the crustal model down to the seismogenic depths of the 2016-2018 Central Italy seismic sequence will be carried out in a following step, integrating the preliminary model with further information (e.g. local earthquakes tomography, thermal and rheological data, grav-mag modeling), the preliminary results also provide some hints on issues that are still a matter of scientific debate, such us the structural style controlling the geological setting in the study area and the role played by structural features inherited from previous tectonic regimes.

### Tectonic stress composition in the Western Ionian revealed by stress inversion of local earthquake focal mechanisms

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Keywords: Seismogenic stress, earthquake location, Ionian Sea.

We analyze an updated dataset of earthquakes of Southern Italy, focusing in particular on hypocenter locations and seismogenic stress distributions in the southern and eastearn offshores of Sicily and Calabria. Using Bayesian non-linear methods for hypocentral locations and hypocenter error estimates we improve the earthquake locations performed by more traditional linearized techniques, and this allows us to make significant progress in the interpretation of seismicity and seismogenic stress distributions especially where seismometric network geometry is more critical. Epicenter maps and hypocenter vertical sections, together with (i) the best quality focal mechanisms coming from seismic waveform inversion and (ii) the orientations of stress principal axes estimated by inversion of focal mechanisms, give us new insight to better recognize the geodynamic engines and plate margin fragmentation in the study area. While several sectors of the study area result to be individually characterized by homogeneous stress distribution and are therefore analyzed with the usual criteria of stress tensor interpretation, others show a marked degree of stress heterogeneity suggesting the overlap of actions by different tectonic engines. We explore the possibility of distinguishing the different tectonic engines acting in these sectors (one of these is western Ionian) by reconstruction of stress inversion results from simulation of different dynamic sources and overlap processes.

### Session S16

### Mediterranean subduction zones: from deep mantle to shallow structure and volcanism

Conveners AND CHAIRPERSONS Claudio Chiarabba (INGV, Roma) Michele Lustrino (Sapienza, Università di Roma) Riccardo Avanzinelli (Università di Firenze)

### The Catalogue of Italian Off-shore Seismicity (C.S.O.) and related hints about the tectonics and geodynamics of the central Mediterranean area

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Keywords: Off-shore seismicity, C.S.O.

In this work we present the preliminary results obtained by the design of an innovative useful tool, the C.S.O. (Catalogo della Sismicità Off-shore, Italian Catalogue of Italian Off-shore Seismicity). The idea of this catalogue has grown up since there is a compelling need, not only for the scientific community, to obtain high-quality locations of the seismicity occurred in the Italian off-shore areas to be correctly addressed to active off-shore tectonic structures.

As well known, the solution of an earthquake location problem has a quality decreasing as the earthquake occur outside of the seismic network and far from the coastlines. The main goal of the CSO is to improve the location quality of the earthquakes occurred in the off-shore domains, reducing uncertainties in location errors. Different tests were produced as a trial-and-error approach, tuning the setting parameters of the location code in order to minimize errors and enhance the accuracy. These preliminary results were obtained using a 1-D average velocity model for the entire dataset, that consistently improved the previous available seismic datasets.

In this study, we investigate the efficiency of the current seismic monitoring system in the central Mediterranean off-shore, computing a refined catalogue that contains about 11,000 earthquakes occurred from 2005 to 2015 in the Adriatic, Ionian, Tyrrhenian and the Sicily channel off-shore domains surrounding the Italian peninsula.

The catalogue is designed with a hierarchical criterion where each earthquake has a unique ID, a direct link to all the earthquake information (e.g. receiving stations, velocity model, P and S phase arrival times, errors, gaps etc.), in order to facilitate its use from several kind of users, even to people not directly connected to research activities.

We also perform a deep analysis of the monitoring performance selecting three test areas where tectonic structures are particularly active and the seismic hazard, potentially connected with anthropogenic seismic hazard, is high. Results show that, although the sensible quality improvement of monitoring achieved in past years, seismicity in the off-shore areas suffers for not negligible errors in locations and the minimum detectable magnitude sharply decreases moving far from the coasts.

### Three-dimensional modeling of Mount Etna volcano: volume assessment, trend of eruption rates and geodynamic significance

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Keywords: 3D modeling, Mt. Etna volcano, emitted volumes.

3D modeling of Mt. Etna, the largest and most active volcano in Europe, has for the first time enabled acquiring new information on the volumes of products emitted during the volcanic phases that have formed Mt. Etna and particularly during the last 60 ka, an issue previously not fully addressed. Volumes emitted over time allow determining the trend of eruption rates during the volcano's lifetime, also highlighting a drastic increase of emitted products in the last 15 ka. The comparison of Mt. Etna's eruption rates with those of other volcanic systems in different geodynamic frameworks worldwide revealed that, since 60 ka ago, eruption rates have reached a value near to that of oceanic-arc volcanic systems, although Mt. Etna is considered a continental rift strato-volcano. This finding agrees well with previous studies on a possible transition of Mt. Etna's magmatic source from plume-related to island-arc related. As suggested by tomographic studies, trench-parallel breakoff of the Ionian slab has occurred north of Mt. Etna. Slab gateway formation right between the Aeolian magmatic province and the Mt. Etna area probably induced a previously softened and fluid-enriched supra-subduction mantle wedge to flow towards the volcano with consequent magmatic source mixing.

### Tracing sediment recycling into the mantle: application of Molybdenum isotopes to ultrapotassic Italian rocks

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Keywords: sediment recycling, Molybdenum isotopes, subduction.

In the last decades the study of non-traditional stable isotopes has provided new means to decipher the contribution of recycled materials in subduction zones and the nature of their transport (i.e., fluids vs. melts).

Molybdenum stable isotopes, thanks to their redox-sensitive behaviour, have been shown to fractionate in superficial environments entailing the formation of reservoirs with very different isotopic compositions. Although the geochemical behaviour of Mo is still not completely understood, it has been suggested that Mo is substantially incompatible during mantle melting although a number of accessory phases (i.e., rutile and sulphides), do retain Mo and can play a role in governing its fate.

It is well accepted that the geochemical and isotopic budget of the subduction-related magmas is strongly dependent on both the nature and composition of the recycled material and the residual mineralogy of the melting process. The coupling between the budget of Mo and traditional trace elements in subduction-related magmas can thus provide useful information on the occurrence of specific residual phases reflecting the composition of the recycled material.

The Italian potassic and ultrapotassic igneous rocks of the Tuscan magmatic province and Mount Vesuvius (Roman magmatic province) show extremely variable and well distinct geochemical and radiogenic isotopic signatures, which are referred to the involvement of different sediment-dominated subduction components in their mantle source. These rocks, thus, represent a unique opportunity to test Mo isotopes as a new tool to tackle the role of different subduction-related components during mantle metasomatism.

In this study we present  $\delta^{98/95}$ Mo and Mo content on these magmatic rocks along with a selection of sedimentary composites as *proxy* of the recycled material. The isotopic signature of these rocks reveals the occurrence of a sort of Italian baseline, with  $\delta^{98/95}$ Mo heavier than other subducted-related magmas measured so far. The absolute Mo content, although significantly different between the two magmatic provinces, is depleted compared to other incompatible trace elements.

The data are discussed aiming to evaluate if the observed differences are due to i) original difference in the down-going sediments, ii) fractionation during sediment subduction and melting in response to different phase stabilisation, and iii) elemental or isotope fractionation *en route* to the surface.

#### Recycled carbonate sediments in the metasomatism of central Mediterranean sub-continental mantle as revealed by mineralogical, chemical and isotopic characteristics of potassic magmatism

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Keywords: carbonate sediment recycling, deep CO2 flux, subduction-related potassic rocks.

Subduction drags a large amount of  $CO_2$  into the Earth's interior, which is partly returned to the atmosphere by arc volcanism. Processes involved in the recycling of subducted carbon within the upper mantle are mainly related to mineralogical transformation during metasomatism. This process can be tracked by the subductioninduced modification of the mantle in term of incompatible trace and major elements (e.g., K, Ca, HFSE), radiogenic and stable isotopes. Potassic and ultrapotassic igneous rocks at destructive plate margin are the result of magmas produced by partial melting of upper mantle that experienced extreme sediment-derived enrichment.

The Central Mediterranean, Italian peninsula and surroundings, is the most important region on Earth for studying subduction-related potassic and ultrapotassic magmatism, derived from partial melting of metasomatised lithospheric mantle wedge The erupted magmas display different potassic and ultrapotassic affinity, from leucite-free to leucite-bearing, with associated shoshonites and high-K calc-alkaline.

Central Mediterranean potassic and ultrapotassic rocks are extremely enriched in incompatible trace elements with variable fractionation of Ta, Nb, and Ti in comparison to Th and large ion lithophile elements (LILE). They are also variably enriched in radiogenic Sr and Pb and unradiogenic Nd. The main geochemical and isotopic signatures are consistent with sediment recycling within the mantle wedge via subduction.

A two-step metasomatism, produced by the recycling of pelitic sediments and dehydration of lawsonitebearing schists, enriched the mantle wedge from which leucite-free ultrapotassic rocks were generated. The involvement of recycled carbonate-rich pelites played an important role in the shift to leucite-bearing ultrapotassic rocks (kalsilite- and leucite-bearing) of the classic 'Roman province'. Such a process is independently demonstrated by minor element contents of high-Fo olivine from Italian potassic and ultrapotassic rocks, and by whole rock isotope data (U-Th disequilibria, Sr-Nd-Pb isotope, and high-precision  $\delta^{238}$ U) on historical K-igneous rocks from Mount Vesuvius. The latter requires the addition to the mantle wedge of U-rich carbonated melts, generated by partial melting of subducted carbonate sediments in the presence of residual epidote. These data provide constraints on the deep carbon cycling within Earth.

#### 3D Architecture and Plio-Quaternary evolution of the Paola Basin: New insights to the Forearc of the Tyrrhenian-Ionian Subduction System

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Keywords: Paola Basin, Tyrrhenian-Ionian subduction system, neutral accretionary-type forearc basin.

The 3D stratigraphic architecture and the Pliocene to Quaternary evolution of the Paola Basin (offshore western Calabria), a segment in the fore-arc of the Tyrrhenian-Ionian subduction system, are reconstructed by using a grid of unpublished of multi-channels, high-penetration, seismic-reflection profiles acquired in the frame of the project SINBUS, integrated by bathymetric data from EMODnet-Bathymetry portal. The Paola Basin is a NNW-SSE elongated, ~ 60 km long and ~20 km wide, slightly asymmetric syncline, which hosted Plio-Quaternary deposits up to 5.5 km thick in its depocenter. The Plio-Quaternary sequence shows an eastward progradational internal geometry that becomes sub-horizontal in the uppermost part. The geometries of deposits suggest that the source area for sediments had to be localized, at first, in the West or North-western sector of the basin, and in the Coastal Chain during the late stage of the basin evolution. Post-Messinian tectonic shortening of reflectors is less than 5% in both the directions of the principal axes of the basin, and thus it is negligible. Tectonic features associated with strike-slip restraining and releasing bends are interpreted along the western sector of the basin. They form a NS-trending and geomorphically prominent ridge separating the Paola Basin from the central sector of the Calabrian margin. The area of the future Paola Basin and its eastern prolongation until the western flank of the Sila Massif was affected by subsidence during and after the Messinian time. At  $\sim 3.5$  Ma, subsidence persisted in the Paola Basin segment, while the area corresponding to the Coastal Chain and the Sila Massif uplifted. As a consequence, a regional scale asymmetrical syncline (Paola Basin) and anticline (Coastal Chain and the Sila Massif) developed. Also, normal faults formed in the hinge zone of the anticline and the Crati Basin nucleated. Based on the wave-length and position of the maximum amount of vertical movements experienced by the fore arc segments affected by subsidence and uplift as well as the lack of significant faults bordering the Paola Basin, the formation of these features could be related at the flexure of the upper plate in response to the subduction system dynamics and sediment load. The strain partitioning into strike-slip fault zones occurred in response to the oblique subduction of the Adriatic-Ionian plate. On the basis of the strike-slip fault zones recognized to the west of the Paola Basin and documented by several authors along the northern Calabrian Arc as well as the lack of significant internal deformation within the sedimentary infill of the Paola basin, the fore arc basin of the Tyrrhenian-Ionian subduction system can be classified as a neutral accretionary-type forearc basin.

#### Volcanism at Slab Tear Faults: the Diamante-Enotrio-Ovidio volcanic complex (offshore north-west Calabria)

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Keywords: Slab Tear Faults, Southeast Tyrrhenian, Volcanic complex.

Several arc-shape sectors form the central and southern part of the Italian peninsula, representing the emerged portion of the continental crust disjoined by slab tear faults (e.g., Olevano-Antrodoco, Ortona-Roccamonfina Tindari-Letojanni faults). These sectors are characterized by different drift velocities and tectonic patterns, while above to them important volcanic phases developed, such as the Vulture volcano (onshore) and the Vulcano-Lipari-Salina alignment (offshore). In the Tyrrhenian basin such kind of volcanism is still poorly investigated and understood though it could be revealed by low-resolution geophysical anomalies and volcanic seafloor morphologies. This is probably due to the fact that this volcanism is characterized by multifarious evolutionary steps, developed and overlapped during its formation since Miocene time. In this work, we present new geophysical data about an unknown intrusive-effusive volcanism affecting a  $40 \times 52$  km large area of the northern part of the Western Calabrian Offshore, about 20 km far the shoreline. The integration of high-resolution multibeam bathymetric data, seismic reflection data, regional magnetic anomalies and local earthquake tomography highlights the volcanic nature of this area, where the Diamante, Enotrio and Ovidio seamounts structure (DEOS) is present. Seismic profiles show that the DEOS developed in an area strongly intruded by volcanics that locally reach the seafloor forming the volcanic edifices. Magmatic mounds and associated structures, which include chimneys and lava flows, are observed within different upper PO sedimentary levels. Three fault systems associated with positive flower structures are identified. They offset both volcanics and sedimentary cover of the Diamante volcano reaching the sea floor, giving place to a set of steep and 1-6 km long scarps oriented between N10°E and N34°E. Moreover, significative magnetic signatures placed in correspondence of northern side of the Ovidio as well as above the Diamante seamounts highlight the presence of deep rooted magnetized volcanic feeding system remnant. The local earthquake tomography further support these findings, revealing beneath the DEOS evidence of gas-filled porosity probably related to magma cooling. The DEOS area lies at the northern boundary of the subducting Ionian slab, at the termination of the Palinuro-Glabro seamounts alignment. We suggest that DEOS represents the easternmost Pleistocene volcanic activity developed along the TF bordering the northern side of the Ionian subducting slab, in proximity of its hinge. We also discuss the overall flat-topped morphology of Ovidio Seamount as the result of the interplay between sea-level fluctuations and subsidence.

#### Intraplate magmatism along the Malatya-Ovacik and Kizilirmak strike slip faults in a post-collisional setting (Central-Eastern Anatolia, Turkey)

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Keywords: Central Anatolia, K-Ar ages, Isotope Geochemistry.

Central-Eastern Anatolia volcanic activity records a long-term geochemical history linked to its geodynamic evolution. The associated magmatism follows the Late Cretaceous to recent compression, due to the convergence and subsequent middle Miocene collision of African and Arabian Plates with Eurasia ones along the Hellenic and Cyprus Arcs to the west, and the Bitlis-Zagros suture to the east. After abundant orogenic magmatism, scattered basaltic volcanism mainly developed in association with the main strike-slip faults of the region namely North Anatolian Fault Zone, East Anatolian Fault Zone and Central Anatolian Fault Zone, in a transtensional tectonic context.

In more detail, in the study area, a middle Miocene volcanic activity was recognized in the Yamadag Volcanic Complex north-west of Malatya, and in the Kepez Dag Volcanic Complex, west of Malatya. Here, the volcanic products, emplaced mainly as lava domes and less numerous lava flows, have calc-alkaline affinity showing the common geochemical and isotopic characters of subduction-related rocks with marked LILE enrichments, very strong Nb-Ta fractionations, high <sup>87</sup>Sr/<sup>86</sup>Sr (0.7039-0.7063) and low <sup>143</sup>Nd/<sup>144</sup>Nd (0.51260-0.51276).

Both tholeiitic and Na-alkaline basaltic products outcrop in the Sarkisla, Kangal and Arguvan areas, postdating calc-alkaline rocks. In Sarkisla, basalts and basanites were emplaced as lava flows during the middle-Miocene (13.9-15.7 Ma) along the Kizilirmak strike slips fault, in the southwestern part of the Sivas Basin. Further to the south, in the NNE and SSE sectors of the Kangal Basin, younger basaltic to trachybasaltic volcanism reached its peak during the Pliocene time (4.8-5.1 Ma). In the Arguvan region, just south of the Yamadag volcanic complex, mostly tholeiitic and rare alkaline lava flows were emplaced during the Pliocene along the Malatya-Ovacik strike slip fault.

Tholeiitic and Na-alkaline rocks of Sarkisla and Kangal are MgO and TiO<sub>2</sub> rich (5.5-13.3-and 1.5-2.2%, respectively), showing small throughs at Nb-Ta, lower LILE contents with respect to calc-alkaline rocks, but a wide range of Sr-Nd isotopic compositions (0.7041-0.7055 and 0.51261-0.51282). Arguvan tholeiitic rocks, on the contrary, are characterized by Th-U peaks, Nb-Ta-Pb throughs, low <sup>87</sup>Sr/<sup>86</sup>Sr (0.7035-0.7038) and high <sup>143</sup>Nd/<sup>144</sup>Nd (0.51285-0.51291).

The late-middle Miocene magmas of Yamadag and Kepez Dag complexes, clearly emplaced in a convergent setting, indicate a derivation from a mantle source modified by subduction components. Tholeiitic and Naalkaline magmas, on the contrary, mark the change from compressional to strike slip tectonic regime at the beginning of the late Miocene. The development of late Miocene Kizilirmak fault and, subsequently, the Pliocene Malatya-Ovacik fault zone favored the passive upwelling of asthenospheric mantle, and the onset of tholeiitic and Na-Alkaline basaltic activity.

#### Morpho-tectonic map of the Tyrrhenian back-arc basin

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Keywords: tectonics, back-arc opening, Tyrrhenian sea.

The Tyrrhenian back-arc basin is a Neogenic basin that opened in response to the E-SE-ward retreat of the subducting Ionian slab under the Apennine chain. To date a large bibliography is available for this basin (Moeller et al., 2014), but un updated morpho-structural map which takes into account the latest multibeam and multichannel seismic data sets is still lacking. Indeed, the structural maps of the entire Tyrrhenian date back to '80/'90. In this work, we present a new morpho-tectonic map of the entire Tyrrhenian basin, from slopes to abyssal plains.

This map results from the analysis of 65 multichannel seismic profiles, several sparker profiles and 200-m-grid cell size bathymetry data. All data were georeferenced and interpreted together using the kingdom package (HIS Markit). In detail, the data sets used are composed by the: CROP profiles acquired in the '90; MS profiles acquired by the OGS during the '60/'80 (<u>http://snap.ogs.trieste.it/</u>); SITHERE profiles acquired for the site survey of IODP leg 107; MEDOC profiles acquired in 2010; and ISTEGE profiles acquired in the 2010. IODP/DSDP wells (Leg 107 and 42A) and crustal velocity information (Prada et al., 2014, 2015; 2018) were used for the seismo-stratigraphic calibration allowing the mapping of three main units: pre-Messinian; Messinian including evaporites; and Plio-Quaternary. This information allowed to constrain the age of faults activity.

Our work results highlight a basin dominated by extension locally overprinted by compression or by transcurrent-motion fault systems. In the western Tyrrhenian, the extension was mostly accommodated by large listric faults forming deep and elongated sedimentary basins. In its eastern (Campania) and southern (Sicily-Calabria) margins the stretching was mainly accomplished through normal faults forming irregular and smaller basins. Furthermore, the central Magnaghi/Vavilov abyssal plain is confined by normal faults that bound the magmatic crust and exhumed mantle rocks (Prada et al., 2016) to continental blocks of the Sardinia-Campania conjugate margins. The Marsili abyssal plain instead is surrounded by fewer, not well expressed, normal faults and, to north and to south, by lithospheric faults (STEP fault).

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### The role of mantle flow on the tectonic and magmatic evolution of the central Mediterranean subduction zone

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Keywords: Subduction, Central Mediterranean, Tyrrheanian sea.

Back-arc extension due to the retreat of the Ionian slab led to the formation of the Tyrrhenian basin that started rifting at  $\sim$ 12 Ma. During this process, pulses of oceanic spreading migrated eastwards, forming the Vavilov and the Marsili basins. The complex geometry and evolution of this subduction zone makes a comprehensive geodynamic reconstruction difficult to achieve. In particular, the link between the tectonic evolution of this area with the changes in mantle flow pattern and volcanism is still poorly understood. I use three-dimensional numerical models of oceanic and continental subduction to investigate this link. Particular focus is put on tracking the mantle flow to understand its role in arc and back-arc magmatism.

Results show that the presence of continental plates (i.e. Africa and Adria) nearby the oceanic subduction of the Ionian slab produces localised deformation within the overriding plate and it is, thus, crucial for the opening of the back-arc basin. During this process the trench retreating velocity dramatically increases for a few million of years. This is associated with an episode of intense melt production of the asthenosphere rising at the back-arc basin. Afterwards, the slab breaks off forming slab windows at the ocean/continent boundaries and causing a second pulse of fast extension. However, the mantle flowing through these slab windows in a toroidal fashion does not have a strong upwelling component and, thus, does not reach the back-arc and arc melting regions. In a different set of models, in which the toroidal flow occurs around the slab edge, and not through a slab window, the mantle is able to rise towards the surface and be involved in the back-arc and arc volcanism. These results are compared to the mantle flow pattern on both sides of the Ionian slab.

## Compression vs. extension during the late Miocene - Pliocene in the Tyrrhenian margin of the northern Apennines: New perspectives from the eastern Island of Elba (Italy)

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Keywords: Northern Apennines, Miocene-Pliocene, tectonic evolution.

The northern Tyrrhenian Sea and the inner northern Apennines (NA) are classically regarded as a late Miocene-Pleistocene back-arc system characterized by crustal extension and acidic magmatism coeval with shortening farther east at the front of the belt. An ongoing debate exists as to whether extension has operated uninterrupted since the Miocene (e.g. Jolivet et al. 1998), or instead transient compressive events have repeatedly punctuated the syn- to post-Miocene regional extensional history (e.g., Bonini et al., 2014). The easternmost Island of Elba is well suited to study the complexities of the Neogene tectonic framework of the inner NA because it exposes a well-preserved section of the orogenic wedge. The nappe pile therein formed by eastward thrusting, stacking and folding of oceanic and continental units from the Eocene down to the Middle Miocene. Well-dated magmatism and contact metamorphism in eastern Elba provides useful insights into the late Miocene deformation timing and mechanisms (e.g. Musumeci et al., 2015; Papeschi et al., 2017).

By relying on recently developed methodologies to characterize and date brittle faults (e.g. Viola et al., 2016) we have generated new age constraints on the tectonic evolution of the Tyrrhenian margin of the NA. The geochronological results, when integrated with new and existing structural and geological considerations, require the critical analysis of the existing geodynamic models and call for alternative scenarios contemplating crustal shortening in the late Miocene early Pliocene that are capable of better accounting for the complex, and now better time-constrained, crustal architecture of this portion of the NA belt.

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#### Calabrian Arc tectonics and mantle sourced diapirism in the Ionian Sea

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Keywords: Calabrian Arc, Subduction complex, Arc orthogonal extension.

Tectonic activity in subduction-rollback convergent plate boundaries commonly involves backward migration of subducting slabs, arc magmatism and plate boundary segmentation. Incipient collision, the presence of indentors and generally lower plate topography may increase complexity and plate fragmentation. Slab tearing plays a major role in developing segmented subduction zones particularly in narrow slab segments, such as the Calabrian Arc, triggering asthenospheric upwelling, dynamic topography and magmatism.

The Calabrian Arc subduction complex in the Ionian Sea is segmented along two oppositely dipping strikeslip/transtensional fault systems, i.e., the Ionian (IF) and Alfeo-Etna (AEF) faults producing deep fragmentation of the Western Ionian domain and the collapse of the accretionary wedge, in agreement with geodetic models suggesting plate divergence in this region. Multibeam and seismic reflection data call for incipient deformation in the corridor between the IF and AEF, marked by buried sub-circular features aligned along the transtensional faults.

Rising material in subduction complexes might be ascribed to different processes and we attempted to discriminate between these processes using magnetic and gravity field data. Magnetic and gravity anomalies are not consistent with a salt/mud compositions of the diapirs nor with a volcanic or magmatic source, in agreement with heat flow data showing a lower than normal thermal regime for the Ionian basin. Gravity/ magnetic modelling best fit was obtained considering the intrusions as serpentine diapirs in agreement with the presence in the Ionian upper mantle of two layers with high seismic P-wave velocity, low S-wave velocity and high Vp/Vs values, interpreted as partly serpentinized peridotites.

Mantle-derived diapirism is not linked directly to subduction processes. The serpentinites, formed probably during Mesozoic Tethyan rifting, were carried below the subduction system by plate convergence; lithospheric faults driving margin segmentation act as windows through which inherited serpentinites rise to the sub-seafloor. Piercing features in the Ionian Sea provide evidence of a new class of serpentinite diapirs within the external subduction system, derived directly from the lower plate. These findings may lead towards a more complete understanding of the structure and nature of the Ionian lithosphere and of the role of inherited serpentinites in driving neotectonics, seismogenesis and plate boundary re-organization in the central Mediterranean Sea.

#### Neogene ultrabasic volcanic rocks in central Urumieh-Dohktar Magmatic Arc (NW Iran): melilitites and nephelinites in subduction setting

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Keywords: Iran, volcanism, UDMA, subduction setting.

About 180 km SW Tehran (central-northern Iran) young (likely The investigated rocks show anomalous mineral paragenesis and whole-rock chemical compositions compared to the other Cenozoic volcanic rocks occurring in Iran. SiO<sub>2</sub> content is extremely low (down to 36.0 wt%), with CaO reaching contents as high as ~19.2 wt%, coupled with generally high MgO (~9.1-13.9 wt%). Alkalis range between ~2.2 and 6.2 wt%, with Na2O/K2O varying from ~0.9 to 8.5. Primitive mantle-normalized patterns show marked troughs at K, Rb and Pb and enrichment in Nb and Ta, resembling typical HIMU-OIB compositions.

The presence of these compositions imply a carbonatitic component in the mantle source, which is uncommon in subduction-related settings, and certainly unique within the entire Cenozoic volcanic rocks of UDMA. Experimental petrology studies in the last decades have demonstrated that carbonated peridotite is able to produce melts characterized by extremely low content of silica but high amount of CaO and MgO (e.g. Presnall and Gudfinnsson, 2005; Hammouda and Keshav, 2015). It is therefore necessary to understand these peculiar rock compositions in order to constrain their mantle source, the role of carbonates and their origin in a subduction-related setting.

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#### Is the Indian eastern margin an ancient Mediterranean coast? - Cartographical experiments with paleopoles

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Keywords: Paleopoles data, GPMDB, Variable radius paleogeography.

The Mediterranean Sea's complicated geological history is still not fully understood, and investigations adopting the expanding Earth geodynamics could be useful to discover previously unnoticed connections among geological and geophysical data and events (Scalera, 2001, 2005, 2012).

A paleogeographical and paleomagnetic experiment has been performed using both synthetic and real plates and relative paleopoles. To made all completely didactic, the behaviour of idealized plates and their poles is made explicit in the case an increase of radius happens. The real plates and their real paleopoles - extracted from the GPMDB for different geological times - are shown on different radius globe.

Focusing on the Upper Triassic period (time of breaking of Pangaea) examples of pole distributions and selections are shown together with problematic situations, like the India plate position alternatives and different possible Pangaea configurations. While Atlantic reconstructions are more easily constrained (at each radius) because the latitudinal elongation of this ocean, the Mediterranean and Tethys can be closed only if a sufficiently smaller radius is adopted. Indian plate appears to have performed strong rotation coming from a full contact of its estearn margin with Angara-Siberian block. This allows us to interpret the Indian western margin as a part of an ever nascent and enlarging "Mediterranean".

In this concept, the eastern Asia must have undergone, from Triassic to Recent, the progressive eastern adding of arc and back-arc terranes (Safanova, 2017). The imperfect closure of Mediterranean in Triassic on lesser radius globes - as constrained by paleopoles - can be related to recent findings of Triassic (Speranza et al., 2012) Ionian basin age and Palaeozoic (Granot, 2016) submerged continental crust under the Herodotus Basin, offshore Cyprus.

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#### The structure of the Calabro-Ionian subduction zone as imaged by high-resolution seismic tomography

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Keywords: Seismic Tomography, Ionian Slab, Lithospheric Tear Fault.

Among the geological features in the Mediterranean region that continue to capture Earth scientists' attention are the subduction processes, since they have a great influence on the tectonic evolution and the geologic structure of the area, as well as on its seismicity and magmatism. In particular, the tectonic framework of the western-central Mediterranean is mostly the result of the NW-dipping subduction of the ancient Ionian oceanic lithosphere, which currently is recognized to be confined beneath the Calabro-Peloritan Arc. With the aim of improving the image of such subduction system and surrounding zones, we performed a detailed 3D image by means of a seismic tomography. We exploited a large dataset of about 20,100 local earthquakes, recorded between 1981 and 2014, and computing algorithms which are able to build a dense grid of measure nodes (LOTOS) and to improve the relative position of clustered events (tomoDDPS). Results show that the slab is in-depth continuous below the southern sector of the Calabro-Peloritan Arc but the deformation processes developing at its edges are leading to its progressive narrowing, influencing tectonics and magmatism at the surface. In particular, along the southwestern slab boundary, where the sinking and the retrograde movement of the slab have caused its segmentation, the deformation is expressed by a combination of a lithospheric vertical tear and a horizontal slab breakoff. The vertical lithospheric tear propagates in the upper plate along a NW-SE fault system (Aeolian-Tindari-Letojanni) up to its tip zone, which has been identified in the Ionian Sea, about 30-40 km off the Sicilian coast; further southeast, lithosphere appears flexed and not broken yet. On the northern side, the slab has been progressively broken parallel to the trench and the horizontal tear may still propagate southwards. Horizontal tearing affecting both the sides of the slab results into a narrowing of the subduction system with consequent stress concentration at the tip zones and enhanced subsidence due to the gravitational pull along the intact segment of the slab. Finally, northwest of Mt. Etna, tomography highlights low V<sub>p</sub> which can be related to an upwelling of deep mantle material likely flowing laterally through the window opened by the complete slab detachment in the western Tyrrhenian Sea.

#### A new technique to estimate fault potential and aftershock forecasts

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Keywords: stress heterogeneity, aftershocks, Coulomb stress.

During the last few decades the implementation of Coulomb stress changes is the main method for explaining the stress transfer hypothesis. The initial enthusiasm of the early 90s for understanding the physics behind aftershock occurrence has faded in recent years as more high-quality data sets make possible broader hypothesis testing that now challenges long-standing ideas about the efficiency of static stress changes. Recent literature supports that the spatial distribution of aftershocks can be explained by the co-seismic fault loading, described by static stress changes. However, observed stress shadows and mismatch between observed and estimated fault planes are often inconsistent with inferred stress changes.. A critical view of Coulomb stress changes framework is required to evaluate how simple assumptions and current triggering concepts affect the success rates of forecast models.

A new technique is presented based on the consideration of the total stress field, taken as the sum of the pre-seismic and the co-seismic stress tensor, and all possible fault planes. Under a positive failure condition we determine the probable planes. We then compare the results for probable and optimally oriented failure planes. In order to illustrate our extended solution space (app. 1M stress estimates per geographical grid point), we use 2D histograms (Euclidean Distance of Strike/Dip vs. Rake), frequently used in DNA sequencing. We use pre-mainshock focal mechanisms, geological fault structures and spatially varying maximum horizontal axis orientation to estimate the regional stress field. We compare estimated and observed 2D histograms to determine if there is at least one common combination of parameters in which the model can reproduce the observed rupture style. We use the new model to answer the questions: (1) Do earthquakes occur on maximum-stressed planes?, (2) How does pre-mainshock stress heterogeneity controls aftershock populations?, (3) How often do aftershock ruptures happen on optimally oriented planes?, (4) How do long-term nucleation probabilities change when we move from an ideal fault zone representation to complex diverse multi-branching fault systems?

We present results from 3 earthquake sequences in California, Japan and Italy, which are known for complex faulting patterns and diversity of aftershocks and foreshocks; the M=7.2 2010 El Mayor-Cucapah and the 2016 Kumamoto. The first along the San Andreas Fault System, marking the continental collision between Pacific and North America plates and the second along a strike-slip fault in a compressional geotectonic area in Kyushu island of Japan. We find a low success ratio (=number of reproduced aftershock ruptures/total number of aftershocks) for optimal planes (0.22-0.35) whereas the new technique which includes heterogeneity in the form of pre-seismic ruptures, reach a high success ratio (0.70-0.82). Furthermore, aftershocks do not usually occur on the maximum stressed faults since this criterion leads to very low success ratios (0.02-0.18). The latter finding has implications for short and long-term earthquake hazard studies, since it shows that critically loaded faults in different times within their loading cycles that may be triggered even with a small stress perturbation in shallow crust. The method can be applied to investigate the effect of stress heterogeneity in subduction zone aftershock sequences.

#### Understanding paleomagnetic rotations in Sicily: Thrust vs. strike-slip tectonics

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Keywords: Paleomagnetic rotations, Sicily, Thrust faults.

The paleomagnetic investigation of the western Sicily Maghrebian belt has revealed since the 1970s that large clockwise (CW) rotations up to 140° with respect to the Hyblean-African foreland occurred synchronous with Tertiary shortening of the chain. The observation that rotations decrease stepwise from internal to external tectono-stratigraphic units led in the 1990s to a widely accepted model postulating that rotational thrust-sheet emplaced during forward orogenic propagation. More recently, other authors suggested that CW rotations from Sicily are conversely the result of late orogenic dextral strike-slip tectonics. Here we report on a paleomagnetic investigation of 30 Jurassic-Eocene sedimentary sites sampled mainly across the WNW-ESE Mt. Kumeta and Rocca Busambra ridges (Trapanese Unit), both bounded to the north by high-angle reverse faults with dextral strike-slip components. We find rotations of 110°-120° at faults of northern ridge margins, that decrease to  $80^{\circ}$ -90° at ~200 m to the south and rise again moving further south. Thus an excess rotation of 20°-40° due to dextral-strike slip shear is annulled to the regional rotational background of the Trapanese Unit at only 200 m from fault traces, translating to paleomagnetically-calculated strike-slip offsets not exceeding 600 m. Further north, seven sites sampled in the Imerese Unit, tectonically stacked above the Trapanese Unit, yield a  $\sim 130^{\circ}$  rotation. Thus our data confirm that CW rotations in Sicily are predominantly related to thrust-sheet emplacement. Strike-slip tectonics has very limited relevance, and gives local rotations that fade out at only 200 m from fault planes.

No differential rotation occurred between the Panormide and Imerese units, both characterized by 130° rotation values and likely representing contiguous paleogeographic domains separated by secondary thrust faults. Considering data from Mt. Kumeta, we constrain at 80° the rotation of the Trapanese Unit. The upper Cretaceous-Eocene Scaglia cover of both Mt. Kumeta and Rocca Busambra records an additional 20°-30° rotation with respect to the Jurassic ridge backbones, implying that it was décolled from the substratum.

Assuming rigid nappe rotations and a rotation pole along the west Sicily coast, we derive (at a 13.5°E longitude) a total 230 km rotational shortening of the chain, and individual nappe displacements in the 20-120 km range, although further non-rotational shortening might have occurred. Thus paleomagnetism definitely represents a proof for the high allochthony of the Maghrebian chain of Sicily, consistently with recent seismic reflection data interpretations. By further assuming that rotations occurred during late Miocene thrusting events in the 12-5 Ma age window (except the Saccense Unit, later stacked onto the foreland), we derive an average 17°/Myr rotation rate, and a paleomagnetically-calculated average shortening rate of 3 cm/yr, that is again consistent with recent geological estimates.

### Session S17

### Geodynamic evolution between the Variscan and Alpine orogeneses: clues from mantle features and magmatic events

Conveners AND CHAIRPERSONS Federico Casetta (Università di Ferrara) Angelo De Min (Università di Trieste) Valentina Brombin (Università di Ferrara)

#### Basic dykes crosscutting the crystalline basement of Valsugana (Italy): new evidence of Permo-Triassic volcanism in the Southern Alps

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Keywords: Basic dykes, Permo-Trias, South-Alpine.

Basic dykes crosscutting the crystalline basement in Valsugana (Southern Alps, Italy) have been investigated for the first time in the framework of the known tectonomagmatic cycles. Petrographic observations and bulk rock analyses suggest a serial affinity variable between calcalkaline (subordinate) to shoshonitic (prevalent), which are generally ascribed to a convergent plate setting. This is confirmed by Sr-Nd-Pb isotopic analyses that display extreme values that are often observed in post-collisional settings. A bulk rock Rb-Sr pseudoisochron suggest an age of the magmatism around 260 Ma, slightly older than that obtained by K-Ar datings that span between 227 and 251 Ma, suggesting that these dykes represent a transition between the Permian and the Triassic volcanic episodes that are known in neighbouring sectors of the Southern Alps. Considering that Permo-Triassic active subduction beneath the South Alpine is scarcely constrained, we ascribe the metasomatism of the related mantle sources to the Variscan cycle, proposing that magma genesis was delayed respect to time of the active subduction. According to recent reconstructions, parts of south-eastern Europe, including the South-Alpine domain, were formed by the break-up of the northern Gondwana margin from the Late Cambrian, in connection with important transtensional movements, leaving rifted continental basins or narrow oceanic seaways. In our view, the subduction processes that induced metasomatism in mantle sources of the South-Alpine region occurred in the connection with the subsequent (Carboniferous?) consumption of lithosphere of these basins, a framework that is compatible with pervasive recycling of continental crust components within the mantle wedge. Then, calcalkaline/shoshonite magmatism was triggered in the Early Triassic by post-collisional extensional tectonics that followed the Variscan orogenic cycle.

#### Plumasite dykes from the Ivrea-Verbano zone: evidence for the triassic magmatism/metasomatism

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Keywords: plumasite, zircon, U-Pb Data.

Plumasite is magmatic rock consisting of oligoclase, corundum (>16 Vol.%), zircon and biotite (Lawson, 1903). Plumasite dykes were reported from different localities of the central Ivrea-Verbano Zone (IVZ, western Alps) as dykes within lower crustal lithologies (Bertolani, 1957). The IVZ is one of the most important exposed lower crustal section characterized by large magmatism and high-temperature metamorphism during Upper Carboniferous - Lower Permian. The intrusion age of the plumasitic dyke is poorly-constrained. Recently, Langone et al. (2017) reported leucocratic dykes, locally plumasitic in composition, intruded within External Gabbro (Finero Mafic Complex, northern IVZ). These dykes show mylonitic fabric, as well as their host rocks. U-Pb zircon data point to an early Permian intrusion age for the Finero plumasitic dykes, followed by partial metasomatic requilibration during Upper Permian, and Lower Jurassic deformation stage. Plumasite dykes have been found in other localities of the IVZ (i.e., Sabbiola Valley, and Alpe Campo). They cut both granulitefacies metamorphic rocks and the gabbroic rocks of the Val Sesia Mafic Complex. The studied samples consist of oligoclase, K-feldpars, corundum and show a well preserved igneous texture: they also contain large zircons from 100 µm to 4 mm in size. Zircon grains were studied on polished thin section. Inspection of the internal structure by cathodoluminescence survey revealed the presence of broad banding zoning typical of zircons segregated by melts. Preliminary U-Pb zircon data obtained by Laser Ablation (LA)-ICP-MS point to a Triassic intrusion age. The possible petrological processes determining the formation of plumasite parent melt will be discussed in order to place further constraints on the comprehension of the geodynamic evolution of the IVZ. The plumasitic composition could be created from a mafic melt that reacted with metamorphic rocks-rich in Al. The presence of plumasite dykes with different intrusion ages in lower crustal rocks of the entire IVZ may suggest that the same melt-rock interaction process occurred at regional scale and at different time.

This project has been also supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 714936) by M. Alvaro.

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#### Permian basic magmatism from Corsica to the southeastern Alps, a new LIP?

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Keywords: Permian magmatism, U/Pb geochronology, Corsica.

Permian Post-Variscan magmatism is known to be widespread in the Alps, in particular within the Southalpine units, where voluminous intermediate to acidic volcanics and basic-ultrabasic intrusive rocks crop out. Here we report new occurrences of basic intrusive rocks from Southern Tyrol (Italy) and western Corsica (France), which may be related to this widespread event. In South Tyrol, a relatively small intrusive body represents the easternmost known occurrence of Permian gabbros. Zircon collected in one of these samples yielded an age of ca. 282 Ma (single zircon TIMS analysis). The geochemical compositions of whole-rocks (including Sr-Nd-Pb isotopes) and minerals (major and trace element data) suggest that these rocks are formed by mantle-derived magmas contaminated by crustal rocks either within the mantle source or during shallow level AFC processes.

Permian basic rocks from Corsica are represented by hundreds of dykes sampled South and East of Ajaccio. Dykes are meter to decameter-thick and yield variable directions (N-S to E-W). Their composition varies from tholeiitic to moderately alkaline and their mineralogy is dominated by plagioclase, clinopyroxene, and rare altered olivine. Sr-Nd-Pb isotopic compositions span a relatively wide range from compositions close to MORB to compositions yielding a marked crustal fingerprint. We report the first ages for these dyke swarms, which yielded zircon U-Pb ages of ca. 282 Ma (laser-ablation ICP-MS data).

Globally, these data support the existence of a large igneous province expanding from the eastern South-Alpine (South Tyrol) to the southern parts of the European continent (Corsica). The densely spaced dykes and the essentially random distribution of the dykes in Corsica may suggest that these dykes mark the region of impingement of a mantle-plume that possibly initiated the magmatism. The geochemical compositions of the basic magmas are however largely overprinted by crustal signatures, which at least in part reflect a mantle source modified (enriched) by recycled subducted material.

#### <sup>40</sup>Ar/<sup>39</sup>Ar geochronology and geodynamic implications of the Cenozoic Southalpine magmatism (North-East Italy)

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Keywords: 40Ar/39Ar geochronology, geodynamics, toroidal/poloidal flow.

Starting in the early Cretaceous, a change in Africa and Europe plate kinematics led to the closure of the Tethys ocean and to the subduction that triggered the Alpine orogeny. During the late phases of orogenesis (Eocene-Miocene) significant magmatic activity affected the Southalpine domain, particularly the effusive to sub-volcanic igneous activity of the so-called "Veneto Volcanic Province" (or VVP). In the VVP, five main volcanic districts can be defined from north-west to south-east: Val d'Adige, Lessini Mts., Marosticano, Berici Hills, and Euganean Hills, characterized by relatively undifferentiated lava (from mela-nephelinites to tholeiites; Beccaluva et al., 2007). Only in the Euganean Hills acidic volcanic and hypabyssal rocks are also present. Here we report the first <sup>40</sup>Ar/<sup>39</sup>Ar radioisotopic ages for the VVP aiming at i) reconstructing the temporal evolution of the Cenozoic Southalpine magmatism and ii) shedding light on the Adria/Europe geodynamic relationships.

The first eruptions occurred in the late Paleocene in the western districts where the magmatism was widespread also during the Eocene (Val d'Adige:  $41.98 \pm 0.20$  Ma -  $40.73 \pm 0.24$  Ma; Lessini Mts:  $45.21 \pm 0.11$  Ma -  $38.73 \pm 0.44$  Ma). During the early Oligocene, both basic and acidic eruptions took place in the Euganean Hills in a time-span possibly shorter than 0.2 Ma ( $32.35 \pm 0.09$  Ma -  $32.09 \pm 0.29$  Ma). Finally, the youngest volcanic products were erupted in the Marosticano district during the early Miocene (~22 Ma).

This magmatism has been generally related to the break-off of the subducted Tethyan oceanic slab and upwelling of mantle diapirs through a slab window after the continental collision at the end of the Eocene (ca. 35 Ma). However, recent high-resolution P wave tomography revealed that the European slab is continuous and nearly vertical. This study allows a re-thinking of the geodynamic models for explaining the VVP magmatism. It is known, the main cause of the origin of the back-arc magmatism is the change affecting the dip of the subducting slab. Therefore, the progressive retreat and steepness of the subducting European slab after the Adria-Europe collision could have created an extensional setting in the back-arc area and induced magmatism in the VVP. Another hypothesis takes into account the mantle material beneath the subducting slab, which escaped laterally and upwelled frontally producing a vigorous toroidal/poloidal flow (i.e., horizontal and vertical rotational vortex-like components of mantle motion). This toroidal/poloidal flow induced melting in the mantle wedge beneath the VVP and triggered the magmatism.

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#### Petrology, geochemistry and geochronology of the Loro Intrusive Complex (Ivrea-Verbano Zone)

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Keywords: Icrea-Verbano zone, U-Pb geochronology, Sr-Nd-Hf isotopes.

The Loro Intrusive Complex is part of the Ivrea Verbano zone and crops out along the Canavese Line in Val d'Ossola. For its location between the northern (Finero type) and the southern (Sesia type) Ivrea Domains, the Loro Intrusive Complex is a key intrusive body to correctly understand the structure and igneous evolution of the whole Ivrea-Verbano Zone. Nevertheless, a detailed and modern petrological and geochronological investigation on this igneous complex is lacking and limited to the work of Boriani (1966).

Diorite and hornblendites are the main lithologies of the Loro Intrusive Complex, even if slices of basement rocks are locally found. Diorites are relatively fine-grained and consist of pargasitic amphibole (60 vol%) and plagioclase (40 vol%) with average An contents of 47 mol%. Strongly altered clinopyroxene (Mg#=0.7) is locally found. Hornblendites consist of brown amphibole and accessory plagioclase. The chondrite normalized Rare Earth Element (REE) pattern of clinopyroxene and amphibole are characterized by a marked light-(L) REE enrichment relative to heavy-(H)REE.

U-Pb geochronology was carried out with LA-ICP-MS on zircon from diorites. Zircons have round shape and under cathodoluminescence are generally homogeneous and rare with ghost zoning. Most of analysed zircons gave discordant U-Pb dates. The few concordant data allowed to calculate a weighted average concordant date at  $274.0 \pm 1.5$  Ma (2s) which is interpreted as the age of intrusion of the dioritic melt.  $\epsilon$ Hf(t) of zircon was measured on the same dated grains with LA-MC-ICP-MS and results range between 0 and +4, thus revealing a significant difference from zircons crystallised from DM mantle-derived melts. Similarly, <sup>143</sup>Nd/<sup>144</sup>Nd(t) and <sup>87</sup>Sr/<sup>86</sup>Sr(t) isotopic ratios of amphibole (0.51240 and 0.70489, respectively) are significantly different from typical DM values.

Geochronological results suggest that the Loro Intrusive Complex is younger than the mafic complex of the southern (Sesia-type) Ivrea Verbano and that is almost coeval with the mafic dike swarms (Appinites; Mulch et al. 2002) found at high crustal level in the Kinzigite Formation in the northern Ivrea Verbano Zone. The trace element, Sr-Nd isotopic signatures of amphibole and the  $\epsilon$ Hf(t) of zircon reveal that the mantle-derived parental melt suffered significant crustal contamination from the host basement, thus preventing inferences on the mantle source.

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### The Predazzo Intrusive Complex (Dolomites, Southern Alps): thermobarometry, oxybarometry and hygrometry of a shallow multi-pulse intrusion

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Keywords: Predazzo, Dolomites, Thermobarometry.

The Predazzo Intrusive Complex (PIC) is the most intriguing remnant of the Middle Triassic magmatic systems of the Dolomitic Area (Southern Alps domain). Almost entirely preserved by the Alpine tectonics, this complex is an ideal laboratory for investigating the physico-chemical conditions of magma intrusion in a crustal context, where numerical modelling can be constrained by field evidence. Although volumetrically limited (4.5 km3), PIC is composed by multiple pulses with K-affinity intruded over a short time span. These pulses correspond to the emplacement of amphibole and biotite-bearing silica saturated (pyroxenites/gabbros to syenites), silica undersaturated (gabbros to syenites) and granitic/syenogranitic rocks. To unravel the T-PfO, and H<sub>2</sub>O conditions of the various intrusive pulses, we developed a multiple approach, based on the concomitant application of "classical" (i.e. specific for intrusive rocks) and "less conventional" methods (i.e. designed for effusive rocks). Such a process allowed the reconstruction of the entire T-P evolution of the PIC magmas, starting from the generation of the main cumulus phases (clinopyroxene) to the latter crystallization of the intercumulus assemblages, mainly made of amphibole, biotite and K-feldspar. A simulation of the progressively evolving melt compositions enabled us to retrieve their T-P-H<sub>o</sub>O paths by means of several thermobarometric, oxybarometric and hygrometric equations (e.g. Burkhard 1991; Anderson 1996; Putirka 2008; Lange et al. 2009; Masotta et al. 2013) and by the application of the Rhyolite-MELTS software (Gualda et al. 2012). In contrast to what proposed in literature, the emplacement of the PIC occurred at shallow depth (< 6 km), in a temperature range of 1000-1100°C to ~600°C and at fO<sub>2</sub> between -0.1 and +0.7 ΔFMQ. H<sub>2</sub>O content of less differentiated magmas varies between 1.0-1.5 and 2.0-2.5 wt%. These results, other than confirming what hypothesized by the field evidence, highlight the peculiarity of this complex, which can be considered a snapshot of a shallow crustal magmatic plumbing system.

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### Long-lasting mantle-derived activity and evolution in the late-Variscan Sàrrabus igneous complex (SE Sardinia, Italy)

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Keywords: Magma differentiation, syn-plutonic mafic dikes, variable stress field.

The Sarrabus igneous massif (400 km<sup>2</sup>), belongs to the Sardinia-Corsica batholith and is a late-Variscan post-collisional intrusive complex occurring in the frontal part of the orogenic wedge. It is mostly made up of Bt-granodiorites and Bt-monzogranites predating late leucogranites. This complex experienced the contribution of several mafic mantle-derived pulses for about 20 Ma. Mafic intrusions are dominated by Hb-gabbroic rocks cropping out for 10 km along the southern coastline, as stretched and dismembered dikes arranged on a general WNW/ESE trend. They were emplaced as forced intrusions -mostly hosted into Bt-granodiorite- surrounded by discontinuous shells of foliated quartz-diorite/tonalite grading to Hb-granodiorite. Mechanical interaction between different terms of a gabbro/tonalitic association is represented by lobate plagioclase xenocrysts and quartz-diorite fragments in gabbroic rocks. Variations in plastic rheological interaction are testified by gabbroic/quartz-diorite interdigitations or by large (up to 4 m) cuspate fragments of mafic dikes into Hbgranodiorites lobes. Mafic magmas experienced (polybaric?) low-pressure crystal/liquid fractionation at depth, as documented by decametric angular fragments of stratified olivine-two pyroxene-bearing gabbroic rocks. Progressive water saturation of mafic magmas is commonly documented by ortho- and clinopyroxene relic cores rimmed by diffuse amphibole growth. A possible plagioclase + amphibole fractionation path ( $\leq 2$  kb) may account for production of quartz-diorite as residual melt. Overall, contrasting characters (e.g., sharp contacts, dark enclaves, color index, plagioclase textures and accessory phases) between Hb-granodiorite associated to mafic rocks and hosting Bt-granodiorite, support a resident -previously mixed- granodioritic magma reservoir, later replenished by mantle-derived magmas. Low-rate of mafic injection favored (1) the stratification at depth and (2) the production of hybrid granodiorites at the upper mafic/felsic magma boundaries. Magma pulses were dismembered during the injection at shallower crustal levels along narrow shear zones. The mafic activity evolved towards diffuse spessartite diking, which records petrographical and geochemical features similar to synplutonic mafic dikes. They are commonly associated to meta- and peraluminous felsic dikes, which represent different crustal end-members. The mafic activity in southern Sàrrabus is related to decompression melting of lithospheric mantle. Sr-Nd isotope data of the late-Variscan whole Sardinia-Corsica mafic activity point to a progressive mantle enrichment southward, possibly inherited from a Pre-Variscan subduction. This magmatic evolution is part of the post-collisional scenario of the Sardinia-Corsica block, marked by its Permian rotation accompanied by a variable stress field. In southern Sardinia this variability is represented by diffuse NNW mafic/felsic dikes switching to NE in central and north-Sardinia.

### Architecture, emplacement mode of late-Variscan plutons and their relationships with post-collisional phases: examples from Sàrrabus igneous massif (SE Sardinia, Italy)

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Keywords: Intrusive zoneography, mantle pulses, transtensional kinematics.

Sardinia is a southern transect of the Variscan Belt intruded by many post-collisional coalescent igneous complexes forming the Sardinia-Corsica batholith. The Sardinian portion of this batholith grew during two main magmatic peaks, clustered at about 305 Ma (Old Magmatic Peak, OMP) and at 285 Ma (Young Magmatic Peak, YMP); plutons intruding different parts of the Variscan basement show different geological styles in terms of emplacement style and mantle/crust contribution. The Sarrabus igneous massif (400 km<sup>2</sup>) is a multi-pulse, composite intrusive complex, occurring in the frontal part of the orogenic wedge in SE Sardinia. It records a complex evolutive history, consisting of several intrusive sequences. The coalescing intrusion are roughly elongated WNW, with sharp sub-vertical contacts. Schematically, the Sarrabus igneous massif consists of a southern part dominated by granodioritic up to monzogranitic rocks related to the OMP, and a northern part made up of leucogranitic rocks referred to the YMP. A continuous contribution of mantle pulses is documented mostly in the OMP. Early mantle-derived products are gabbrotonalites exposed close to the northern contacts with the host basement; these mafic intrusives occur as a homogeneous sills or masses dismembered by YMP leucogranites. A further mafic pulse consists of disrupted sub-vertical, syn-plutonic, gabbroic dikes associated with quartz-diorites, which are well exposed along the southern Sàrrabus coastline. These dismembered dykes, scattered within the granodiorite with a general WNW trend. The mafic activity evolved towards diffuse diking (mainly spessartites), which resulted in several NNW trending dike swarms that crosscut the OMP intrusives with cool, sharp contact. Spessartites are the latest episodes referable to the OMP; they are frequently associated to metaluminous and garnet-bearing peraluminous felsic dikes and stocks. A subsequent generation of olivine plagioclase -phyric mafic dikes with tholeiitic signature crosscut the YMP. The resulting scenario suggests a northward growth of Sarrabus igneous massif, accompanied by (1) bimodal character of this magmatism; (2) increasing contribution of crustal melts and a progressive decrease of mantle/ crust interactions; (3) progressive shallower emplacement conditions. The late NS trending dyke swarm, which emplaced in dilational jogs accounts for a NS  $\sigma_1$  stress field affecting the entire southern Sardinia lithosphere during Permian time. Conversely, the emplacement of the OMS intrusions and the related dismembered mafic bodies and dykes were controlled by a possible WNW transtensional kinematics. On a larger scale, this variability of stress field, joined to crustal inhomogeneity, could account for different mechanisms of magma ascent and decompression melting that result in different rock associations and petrological signatures.

# The Val Biandino Intrusive Complex (central Southern Alps, N Italy): New geochronological and geochemical data on the Permian magmatic activity in the Southalpine domain

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Keywords: Permian magmatism, crustal anatexis, Val Biandino Intrusive Complex.

We present here new geochemical and geochronological data on the Val Biandino Intrusive Complex (VBIC) and the San Biagio granite, two poorly known magmatic bodies located in the central Southern Alps (Valsassina, Lecco). The Variscan hosting basement of these intrusive rocks consists of two mica metapelites and metapsammites, with minor amphibolite lenses.

The main stock of the VBIC mainly consists of high-K calcalkaline peraluminous qz-diorites, with minor metaluminous to slightly peraluminous high-K calcalkaline gabbro-diorites and granodiorites. Highly peraluminous leucogranites occur as small lenses and dikes crosscutting the mafic-intermediate masses. The San Biagio granite, cropping out to the north of the VBIC, has high-K calcalkaline affinity and a peraluminous character. Our new SHRIMP U-Pb analyses on zircon grains from the VBIC leucogranites and the San Biagio Granite constrain their emplacement at 289 and 285 Ma, respectively. Geochemical data suggest that the various rock types are not co-magmatic, despite they intruded in close space and time. This interpretation is supported by several line of evidence: (1) the compositional gap occurring in the major element variations diagrams with increasing SiO<sub>2</sub>; (2) the highest LILE, the lowest HREE and HFSE, but similar LREE contents in the gabbrodiorites with respect to leucogranites; (4) a genetic link through fractional crystallization processes may be excluded due to the absence of liquid line of descent between gabbro-diorites and leucogranites. On the other hand, fractional crystallization seems to be the main cause of the observed compositional variation within the same rock type, even if within a small silica range. The described lithological and geochemical features of the VBIC strongly resemble those of other Permian intrusive complexes in other sectors of the Southalpine domain, with a particular affinity with plutons located east of the Giudicarie Fault (e.g. Cima d'Asta, Ivigna, Brixen), suggesting similar genetic processes.

In our interpretation the VBIC rock varieties likely represent different batch melts generated by melting of a heterogeneous continental crust. Based on a comparison with experimental data, a lower crustal amphibolebearing metabasalt, probably enriched in  $K_2O$ , is a likely source rock for the qz-diorites. The granodiorites show low Rb/Sr (<0.6) ratios and are probably generated by partial melting of meta-igneous (intermediate) sources by amphibole dehydration melting. Most of the leucogranites display higher Rb/Sr ratios (>1) and are most likely generated by biotite dehydration melting of heterogeneous upper crust. The high-thermal regime, developed during the Early Permian rifting phase at the end of the Variscan orogenesis, was responsible for this phase of crustal anatexis, as also testified by the occurrence of migmatitic and granulitic units of Permian age in several areas of the Alps.

#### From Variscan to Alpine tectonics: magmatic and metamorphic evolution of the Argentera-Mercantour dioritic dyke swarm

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Keywords: Late-Variscan magmatism, External Crystalline Massifs, Western Alps.

In the Argentera-Mercantour Massif (External Crystalline Massifs, ECMs) Variscan migmatites and late Carboniferous granites are crosscut by a dioritic dyke swarm. More than 60 years after the first report (Faure Muret, 1955), these dykes have been mapped in detail at Valscura and Val du Boréon, located, respectively, N and S of the main post-collisional granitic pluton, the "Central Granite".

NE-SW trending and steeply dipping dioritic dykes show chilled margins and degassing bubbles, while, in the innermost parts, soft contacts and magmatic breccias mark the boundary between different igneous types, testifying a complex intrusive history. As inferred by whole rock and EMPA analyses, these dykes are magnesian, calc-alkalic to alkali-calcic, and peraluminous; an alkaline affinity only for the latest magmatic pulse is otherwise suggested by amphibole composition. Intrusive structures and textures indicate a shallow emplacement level, consistently with the sub-aerial condition locally experienced by the Argentera-Mercantour basement from late Carboniferous to Lower Triassic. Thermobarometric estimates on the first metamorphic assemblage developed within these dykes (T $\sim$ 300°C, P<0.1 GPa), and interpreted as related to a post-magmatic hydrothermal system not affecting the host rocks, confirm the shallow intrusion. At a later time, dykes were intersected by the mylonitic shear zones that reworked the massif during the Alpine cycle: syn-kinematic mineral assemblages within dykes confirm the metamorphic peak conditions already inferred for this tectonic event (Sanchez et al., 2011).

The occurrence of this dioritic dyke swarm implies an extension of the magmatic activity in the Argentera-Mercantour Massif beyond the Permo-Carboniferous boundary: intrusives similar in field relationships and compositions are not yet known in the other ECMs (Debon &Lemmet, 1999), but are commonly reported in other parts of the southern European Variscan belt (e.g. Bonin et al., 1998). Moreover, thermobarometric constrains on metamorphic assemblages have allowed for the first time to define a P-T-d-t path relating to the Alpine evolution of Argentera-Mercantour Massif that include both prograde and retrograde stages.

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#### The Triassic sills of the Costabella Crest (Moena, TN-Italy) in comparison with coeval Dolomitic magnatites

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Keywords: Triassic magmatism, Dolomites, Geodynamical costraints.

The trigger of the Triassic magmatism in the Eastern Alps (about 235 Ma) is still highly debated, and both extensional and compressional theories are invoked. The first is mainly supported by the related extensional geologic structures, while the second family of theories is supported by the chemistry of the better exposed lithotypes and the high sedimentation rate, typical of a back-arc environment, whose arc is supposed to be located east or south of the Adria Plate. We support a not orogenic genesis for the dolomitic Triassic magmatism due to the presence of coeval magmatic products showing not orogenic features, by the position of such magmatic province during Triassic times (edge of the Intra Pangea Dextral Shear; IPDS) and by the sedimentation rate which appears comparable with that of the North America Atlantic coast located along the IPDS. It is interesting to notice that the IPDS, which probably begun to move in early Permian, started its extensional movement 235 My ago. In this work we mainly attempt to evaluate possible interaction of the magmatic products with the carbonate (host rocks) through the study of the sills located in the Costabella Crest (Moena, TN Italy), and with the comparison with other dolomitic Triassic products, then, to give a small contribute about the geodynamic discussion.

Generally, the samples show ipoialine to strong porphyric textures and a variable grade of alteration mainly due to disequilibrium between olivine and the melts in the magmatic chamber. In the Total Alkali Silica diagram the sills fall in the alkaline field (from basanite to tefriphonolite), but this partially contrasts with their paragenesis. Indeed, among the phenocrystals the plagioclase appears very abundant and show a bimodal composition (labradorite and anorthite). Carbonates can be present with primary textures to suggest the presence of small amount of carbonatic melts in the magma chamber possibly explaining the isotopic features found in the dolomitic flows where a strong isotopic Sr variability is associated to small Pb and Nd isotopic ones. Apart the strong interaction with the host rocks and the post-emplacement alterations, three groups with different La/Yb ratio can be recognized suggesting a heterogenic source. Finally, to evaluate the supposed subduction-related chemical features, as the negative Nb anomaly, the Triassic samples have been compared with other not arc related magmatic products placed along the IPDS of the Central Atlantic Magmatic Province emplaced at the TJ boundary. Despite the very different grade of alkalinity, locally their incompatible element pattern shows strong similitudes that we relate to past subductions.

#### New insights into the Post-Variscan evolution of the northern Ivrea-Verbano zone (Finero complex, southern Alps)

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Keywords: Subcontinental Mantle, Lower Continental Crust, Magmatic Underplating.

The Ivrea-Verbano Zone (IVZ, Southern Alps) is a well-known section of lower continental crust, where km-scale subcontinental mantle bodies crop out in proximity of the boundary of the Adria plate, corresponding to the Insubric line. Detailed mapping demonstrated that the mantle peridotites in the central IVZ were lenses tectonically interfingered with amphibolite to granulite-facies metamorphic rocks prior to the intrusion of the Upper Carboniferous-Lower Permian Mafic Complex, namely during the Variscan orogenic cycle or before, likely as part of an accretionary wedge.

Ongoing studies in the northernmost part of the IVZ (i.e. the Finero Complex) highlights further complexity. This domain is a tectonically-thinned section of the lower crust consisting of three tectonic units: 1) the structurally deepest unit has a lens shape and consists of the Phlogopite Peridotite mantle unit (PP), which is surrounded by mafic-ultramafic intrusive rocks of the Layered Internal Zone (LIZ) and by the Amphibole Peridotite (AP); 2) the intermediate unit (External Gabbro, EG) is made of deformed meta-gabbros/diorites and is bounded by ductile shear zones; 3) the shallower unit consists of amphibolites-facies basement rocks (Kinzigite Formation).

The PP mantle unit was pervasively metasomatised by peculiar K-LILE-rich melts with large crustal component and successively intruded by Triassic alkaline melts. The contact between the PP unit and the mafic intrusives is gradational and is characterized by a magmatic fabric in the mafic intrusives coherent with the solid-state deformation fabric of the peridotites. The LIZ and AP units record a large number of magmatic pulses related to both LREE-depleted and LREE-enriched melts, which were accompanied by variety of meltrock reactions. As whole, the data suggest that the PP-LIZ/AP transition acted for a very long time as primary lithospheric discontinuity, representing a preferential level of channelling of uprising melts.

The U-Pb system of PP zircons records different thermal perturbations, which imply that the mantle sequence remained at high-T conditions until 190-180 Ma (Zanetti et al., 2016). The exhumation was driven by high-T shear zones, like those that form the tectonic boundary between AP and EG, during extensional stages that thinned the continental crust over an extended time interval (230-180 Ma; Langone et al., 2018). Later extension was focused westward, leading to the opening of the Jurassic Alpine Tethys.

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# Session S18 The nature of the crust-mantle transition and its effects on the regional tectonic and magmatic evolution

Conveners And Chairpersons Roberto Braga (Università di Bologna) Valentina Magni (UiO, Oslo) Claudio Natali (Università di Ferrara)

#### Petrology of the Rocca d'Argimonia ultramafic sequence (Ivrea-Verbano Zone): implications for the evolution of mantle melts intruding the lower continental crust

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Keywords: lower continental crust, peridotite-pyroxenite intrusion.

We present a preliminary petrological investigation of the Rocca d'Argimonia peridotite-pyroxenite sequence, which intrudes the lowermost continental crust of the Ivrea-Verbano Zone (South Alpine domain). This ultramafic sequence is up to 400 m thick and is enclosed within gabbronorites from the southern-western sector of the Ivrea Mafic Complex. The main purpose of this study is to unravel the magmatic evolution that gave rise to the peridotite-pyroxenite sequence.

The peridotites are mostly amphibole-bearing dunites that are locally characterized by poikilitic orthopyroxenes (~1 cm in size). The pyroxenites are amphibole-bearing olivine websterites to plagioclase-bearing websterites, with modal orthopyroxene/clinopyroxene ratio >1. Hornblende gabbronorite dykes (up to 15 cm thick) locally crosscut the peridotites and show mm-scale thick, amphibole-bearing orthopyroxenite reaction zones along the contact with host rocks. Peridotites, pyroxenites and gabbronorite dykes typically show nearly polygonal textures, which locally preserve hypidiomorphic magmatic structures. Application of the Ca-in-Opx and Opx-Cpx geothermometers to the peridotites and the olivine websterites gave temperature values ranging from 720 to 810 °C. These estimates most likely reflect slow cooling and recrystallization of the ultramafic sequence in the lower continental crust.

The whole-rock chemical compositions of peridotites, pyroxenites and gabbronorites do not represent frozen melts. The Mg# [Mg/(Mg+Fe<sup>2+</sup>)] decreases from dunites to pyroxene-bearing peridotites, olivine websterites and plagioclase-bearing websterites, and these Mg# variations are paralleled by olivine, pyroxene and spinel compositions. In addition, the Al content of pyroxene and spinel roughly increases with decreasing Mg#, thereby suggesting formation of the peridotite-pyroxenite sequence in response to a plagioclase-free fractional crystallization process. In particular, the following crystallization order could be envisaged: (1) olivine, (2) olivine + pyroxene, (3) pyroxene. The poikilitic structure of orthopyroxene however argues against the stage (2), coeval crystallization of olivine and orthopyroxene. Furthermore, the forsterite vs. NiO variations of olivine are not fully consistent with a magmatic evolution controlled by fractional crystallization alone. Hence, the olivine-poor and the olivine-free ultramafic rocks could also form by olivine-consuming melt-dunite reactions, namely reactive migration of the melts feeding the gabbronorite dykes into an olivine-rich matrix. Trace element and isotopic analyses are currently in progress to establish the extents of the fractional crystallization and reactive melt migration processes, and to elucidate the potential process of melt contamination by the gabbronorites hosting the ultramafic sequence.

#### Kimberlite-borne pyroxenite xenoliths: Samples of cratonic crust-mantle transitions?

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Keywords: continental crust, arc cumulates, lithosphere.

Along with mantle eclogites, pyroxenites form an integral part of the xenolith inventory found in cratonic kimberlites, but compared to eclogites, which have Archaean to Palaeoproterozoic ages and are typically interpreted as ancient subducted oceanic crust (Aulbach & Jacob, 2016), pyroxenites have not been systematically investigated. Pyroxenites (sometimes referred to in the literature as high-Mg eclogites) are distinguished from eclogites by the low jadeite content in clinopyroxene, which is in part thermally controlled. However, the highly diverse mineralogy and elemental composition of pyroxenite xenoliths suggests a variety of origins. Petrographically, they range from isolated garnet grains or garnet "necklaces" in a matrix of modally dominant, texturally equilibrated clinopyroxene  $\pm$  orthopyroxene to roughly equal proportions of garnet and clinopyroxene resembling mantle eclogites. Compositionally, they are characterised by high MgO, Cr<sub>2</sub>O, and TiO<sub>2</sub>, and low FeO, Al<sub>2</sub>O, and Na<sub>2</sub>O contents. Their proposed origins range from (1) picritic (MgO-rich), littledifferentiated ancient oceanic crust, (2) products of hybridisation of eclogite-derived melt with peridotite, and (3) products of metasomatic interaction with ultramafic melts to (4) crystallisation products near the oceanic or continental crust-mantle boundary (Aulbach & Jacob, 2016). Cumulate formation in deep arc crust has been proposed to not only explain the broadly andesitic composition of continental crust (Lee & Anderson, 2015), but also its oxidised nature and Cu-Eu deficiency (Tang et al., 2018). In addition, the deep recycling of such cumulates by delamination may in part be responsible for the elemental and isotopic heterogeneity observed in convecting mantle sources (Tatsumi et al., 2014). A combination of elemental and isotopic criteria will be applied to published data sets in order to identify pyroxenites from on- and circum-cratonic settings that may represent cumulates originally formed at moderate pressures, estimate their densities, and investigate their potential significance to ancient continental crust formation and to the generation of geochemically distinct sublithospheric reservoirs.

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### Formation of replacive olivine gabbros in the Oman Moho Transition Zone: Geochemical evolution during deformation-driven dunite impregnation

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Keywords: Replacive formation, Dunite-olivine gabbro layering, Melt-rock interaction.

Recent studies investigate the replacive formation of gabbroic lithotypes from mantle-related protoliths in the oceanic lithosphere and the compositional evolution of the percolating melt and pre-existing matrix during melt-rock interaction processes (Basch et al., 2018). The hundred-metre thick Oman Moho Transition Zone formed of a layering of interfingered dunites and variably evolved olivine gabbros is an ideal case study of the possible extent of geochemical evolution of the melt and percolated matrix during melt-rock interaction processes, in a melt-focussing system. Higgie & Tommasi (2012) recently demonstrated the replacive origin of the olivine gabbro layers, formed during open-system reactive percolation within the pre-existing dunite, progressively corroding the olivine matrix and crystallizing clinopyroxene and plagioclase. The decreasing modal composition of olivine (from 95 vol% to 10 vol%) is accompanied by a change in symmetry of olivine Crystallographic Preferred Orientation from axial-[100] patterns in the dunite to axial-[010] CPO in the olivine gabbro layers (<50 vol% olivine), indicative of the higher cumulated strain and melt/rock ratio integrated over time in the *olivine gabbro layers*. This structural evolution is well correlated with strong geochemical discrepancies analyzed between olivine-rich layers (>50 vol% olivine) and olivine gabbro layers (<50 vol% olivine). The olivine-rich layers show constant Forsterite contents in olivine (Fo = 88-89 mol%) and Mg-value in clinopyroxene (Mg# = 88-90 mol%) at varying Anorthite contents in plagioclase (An = 82-90 mol%), indicative of reactive crystallization at decreasing melt mass and buffering of the melt composition by the matrix and the melt-rock interaction process. The *olivine gabbro layers* show constant mineral major and trace elements compositions of olivine (Fo = 84-85 mol%), clinopyroxene (Mg# = 86-88mol%) and plagioclase (An = 87-90 mol%), indicative of small degrees of melt fractionation during opensystem reactive percolation, and therefore mineral compositions dominated by the percolating melt. This combined structural and geochemical study demonstrates the possible complete assimilation of the protolith during continuous reactive percolation processes, as well as the important control of the melt-rock ratio integrated over time (and therefore of the open-system vs closed-system percolation style) on both the preexisting structure and geochemical compositions inherited within the replacive lithotype.

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### The bimodal basalt-rhyolite suites of the Paranà CFB province: a reappraisal of the petrogenesis and tectonomagmatic significance

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Keywords: Basalt-rhyolite, CFB, Parana.

Normal 0 14 false false false MicrosoftInternetExplorer4. The Paranà Continental Flood Basalt (CFB) Large Igneous Province (LIP) of eastern south-America mainly consists of voluminous High-Ti (HT) and low-Ti (LT) basaltic suites erupted as precursors of the continental break up and opening of the South Atlantic Ocean in Lower Cretaceous, A bimodal rhyolite-basalt association, concentrated toward the South Atlantic margins, is observed with rhyolites generally laying at the top of the CFB sequence. Rhyolitic rocks are classically subdivided into predominant low-Ti (LT, dacite-rhyolite Palmas-type) and subordinate high-Ti (HT, trachydacite Chapeco-type) groups, which share the same geochemical features (Ti and other incompatible element) with the underlying basalts. The most popular petrogenetic interpretations for the Paranà rhyolites s.l. deal with: 1) re-melting of underplated CFB (Bellieni et al., 1986); 2) a more complex model with LT rhyolites generated by shallow level assimilation-fractional crystallization processes from LT basalts, whereas for HT rhyolites a genesis by partial melting of underplated HT basalts is preferred (Garland et al., 1995). A critical re-examination of the available data leads us to infer that both LT and HT rhyolitic rocks could be generated by fractional crystallization processes from the respective underlying basalts. Fractionation modes for the two types appear, however, distinctly different: LT dacite-rhyolites could be generated in shallow magma chambers where they underwent significant crustal assimilationù -as indicated by their isotopic signatures- and were erupted mainly as extensive rheoignimbrites and thick lavas (up to 600 m total thickness); HT trachydacites do not show, instead, evidence of crustal assimilation (the isotopic features perfectly overlap those of HT basalts) and their generation is compatible with continuous fractional crystallization during rise through crustal fissures, as indicated by their high degree of porphyricity and emplacement mainly as lavas and dykes. These differences in fractionation styles between LT and HT silicic magmas could reside in the comparatively lower silica saturation and higher temperatures of the HT suite, resulting in a lower viscosity thus preventing significant ponding at crustal levels. The generation of rhyolitic magmas by fractional crystallization from the underlying basalts appears to be a common petrogenetic process in most CFB LIPs, particularly in the Gondwana realm, marking the inversion of the stress regime from regional extension due to lithosphere doming to localized continental rifting as a precursor of oceanization.

#### Peridotite xenoliths from Cofrentes (Spain): inferences on mantle domains interlayered at crustal depth

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Keywords: Mantle xenoliths, geothermometers and geobarometers, MOHO depth.

The Iberian Peninsula is characterized by the outcrops of significant alpine-type peridotite massifs both in the Betic and the Pyrenean orogenic belts, ophiolitic peridote occurrences as well as by several volcanic centres entraining mantle xenoliths (Bodinier & Godard, 2014, Ancochea & Nixon, 1987), allowing a multiple outlook of deep mantle processes occurring in the region.

Mantle xenoliths, such as those from the volcanic districts of Calatrava (central Spain), Olot (south-east Spain) and from the Betic locality of Tallante were extensively investigated by various petrological studies, whereas those of the volcano of Cofrentes have been reported, but so far never investigated in detail. They represent a mantle section located between the Betic and Pyrenean belts, in a sector faulted and deformed at least since the Mesozoic (Villaseñor et al., 2018). The study of these xenoliths is therefore very important to complete the lithospheric mapping of the Iberian region. Xenoliths from Cofrentes are extremely fresh, but rarely exceed 1-2 cm in size. Thin section observation, coupled with in situ-major and trace element analyses, show that they are spinel-bearing peridotite characterized by protogranular textures. Using an iterative method that combines the T-P results calculated with various geothermometers and geobarometers, calibrated for ultramafic systems, we obtained that all samples record equilibration temperatures in the range of 610 to 930 °C, and pressure from 13 to 7 Kbar.

The xenoliths from Cofrentes, if compared with mantle xenoliths from other Iberian localities (and more in general with xenoliths from other volcanic districts of the circum-Mediterranean area studied by our research group) display the lowest equilibration temperatures, thus suggesting a provenance by a mantle domain equilibrated at relatively shallow conditions, as confirmed by the pressure values. Therefore, it appears that the MOHO beneath Cofrentes is shallower than beneath other volcanic districts, and/or that significant slivers of mantle rocks penetrated at crustal level, a process that has to be explained within the geodynamic evolution of the Iberian margin that was affected by multiple extensional and compressional phases.

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### The role of crustal assimilation in the genesis of the Middle Triassic Predazzo Intrusive Complex (Dolomites, Southern Alps)

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Keywords: Predazzo Intrusive Complex, Dolomites, Crustal assimilation.

The Predazzo Intrusive Complex is a 4.5 km<sup>3</sup> multi-pulse ring-shaped pluton emplaced during the Middle Triassic magmatic event in the Southern Alps domain. It is almost completely preserved from the Alpine tectonics, and this feature, together with its compositional variability, made it an intriguing study case since the beginning of the 19th century. The complex is constituted by three magmatic pulses (Shoshonitic Silica Saturated, Shoshonitic Silica Undersaturated and Granitic Unit) emplaced in a short time span, and ranging in composition from gabbroic/pyroxenitic to syenitic/granitic. It intrudes the Permo/Triassic sedimentary sequences as well as the Permian ignimbrites of the Athesian Volcanic District. The relationships with the related volcanic sequences and the host rocks, strengthened by thermobarometric calculations, suggest a shallow depth of intrusion. Debated is instead the geochemical variability of its magmatic suites, as well as their orogenic signature. Whole rock Sr-Nd isotopes, corroborated by EC-AFC (Bohrson & Spera 2001) numerical simulations enabled us to discriminate between the mantle signature and the (possible) interaction of the Middle Triassic magmas with the crust, whose components are the Triassic carbonates, the Permian intrusives and rhyolitic ignimbrites, and the Kinzigite Fm. (Voshage et al. 1990; Sinigoi et al. 2016). Results showed that the Predazzo Intrusive Complex magmas plot in the enriched mantle source field, enhancing the presence of a subduction-signature component in the mantle beneath Southern Alps during Triassic. EC-AFC models indicated the presence of distinct geochemical signatures for the magmatic suites, as well as a slight degree (5-6%) of crustal assimilation by magmas, which mainly differentiated by means of fractional crystallization processes.

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## Carbon-rich fluids infiltration into the mantle-wedge: from early carbonate inclusions to late veins in orogenic peridotites from the Ulten Zone

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Keywords: carbon metasomatism, mantle-wedge, Ulten Zone.

COH-fluids released by the subducting slab in a collisional setting can induce carbonation of mantle-wedge ultramafic rocks. Lithospheric mantle can therefore store a fraction of slab-derived CO<sub>2</sub>, and processes such as de-carbonation and carbonate dissolution play a major role in mobilizing carbon in a subduction system (Frezzotti et al., 2011). Despite this, the carbon transfer into the mantle-wedge is poorly constrained (Kelemen & Manning, 2015). Here, we report petrographic features combined with chemical analyses of carbonate minerals in orogenic peridotites from the Ulten Zone (Eastern Alps). Coarse-grained spinel peridotites and fine-grained garnet-amphibole peridotites underwent multi-stage metasomatism caused by infiltrating COH-fluids. Clues of carbonation and de-carbonation are provided by the occurrence of different generations of carbonates in different microstructural domains. Included ferroan dolomite ( $X_{FeCO3} \approx 0.02$ ) in Cr-spinel  $(Cr/(Cr+Al) \approx 0.43)$  in a fine-grained peridotite testifies that the onset of carbonation processes occurred in the spinel stage. Further input of fluids at peak conditions in the garnet stability field led to precipitation of a second generation of dolomite, occurring as interstitial grains in the peridotite matrix. During exhumationrelated retrogression, interaction of the peridotites with late serpentinizing fluids promoted CO, release due to dolomite de-carbonation, whose microstructural evidence is provided by calcite + brucite aggregates as pseudomorphs after dolomite (Förster et al., 2017). In-situ EPMA measurements on dolomite inclusion associated with calcite + brucite reveal an increase of the Sr concentration from early dolomite to calcite (1807 to 2120 ppm). These Sr values suggest the crustal origin of infiltrating carbonaceous aqueous fluids. The latest metasomatic event promoted the formation of vein carbonates, i.e. dolomite and calcite associated with tremolite, chlorite and chrysotile/antigorite, crosscutting the matrix of slightly to highly serpentinized fine-grained peridotite. In summary, the new data on carbonate-bearing Ulten Zone peridotites indicates a prolonged supply of COH-fluids carrying crust-derived elements during the whole metamorphic evolution of these rocks, and allows to unravel means of carbon mobilization and storage in the mantle-wedge.

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#### Metagabbros, meta-monzogabbros and metabasites from Serre Massif (Calabria-Italy): evidence of a Neoproterozoic magmatism at crust-mantle transition

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Keywords: Metagabbros, metabasite, metamonzogabbros.

Different types of Variscan mafic granulites characterize the lower crust of the Serre Massif (Calabria, Southern Italy). They consist of: layered metagabbros (Pl+Opx+Amph±Cpx±Bt±Qtz±Grt), metric bodies of meta-monzogabbros (Pl+K-feld+Opx+Cpx+Bt±Qtz±Grt) and lenses or layers of metabasites (Pl+Opx+Cpx±Bt±Amph±Qtz±Grt) interleaved the overlying migmatitic metapelites and felsic granulites. The Variscan metamorphic events developed in high grade metamorphic conditions in which partial melting and fluid interaction were effective (Fornelli et al., 2011, 2014). However, the whole chemical composition of mafic granulites seems unmodified because migrations of melts at large scale have not been documented. Therefore, the whole rock compositions of granulite mega-samples can give suggestions about the magmatic history of their protoliths.

Geochemical data indicate a mantle origin for the Neoproterozoic magmatic protoliths (~570 Ma, Fornelli et al, 2011). Metagabbros and metabasites show sub-alkaline features (Na<sub>2</sub>O+K<sub>2</sub>O=1-5%) with K<sub>2</sub>O<1%, whereas meta-monzogabbros display alkaline character (Na<sub>2</sub>O+K<sub>2</sub>O=5-7%) with K<sub>2</sub>O around 3% testified by Bt and K-feld. In metagabbros, the <sup>87</sup>Sr/<sup>86</sup>Sr <sub>(570 Ma)</sub> ratio ranges from 0.703 to 0.708 with low values of <sup>87</sup>Rb/<sup>86</sup>Sr (from 0.001 to 0.024). Metabasites have higher <sup>87</sup>Sr/<sup>86</sup>Sr <sub>(570 Ma)</sub> values (0.707-0.710) with <sup>87</sup>Rb/<sup>86</sup>Sr ratio from 0.025 to 0.237 Meta-monzogabbros show <sup>87</sup>Sr/<sup>86</sup>Sr <sub>(570 Ma)</sub> ratio around 0.705 with high <sup>87</sup>Rb/<sup>86</sup>Sr (0.489-0.544). The  $\varepsilon_{Nd(570 Ma)}$  varies from 4.902 to -0.843 in metagabbros, from 0.741 to -2.388 in metabasites, whereas in meta-monzogabbros assume the values varying from -1.078 to -1.253.

The meta-monzogabbros show a strong mantle affinity but are enriched in incompatible elements, their origin seems linked to small degree of enriched mantle melting. The metagabbros and metabasites show crust-mantle interaction for their initial <sup>87</sup>Sr/<sup>86</sup>Sr and  $\epsilon$ Nd<sub>(570 Ma)</sub> values. We hypothesize that subsequent and incremental partial melting events (after the production of gabbroic magma) produced mantle melts with tholeiitic and calc-alkaline affinities migrating in the overlying metasedimentary crust; the stay in hot lower metasedimentary crust induces a certain grade of crust contamination charged by crustal fluids or melts, evidenced by the increase of initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio and by decrease of  $\epsilon$ Nd<sub>(570 Ma)</sub> values at least in protoliths of metabasites. On the other hand, the placement of metabasites within metasedimentary crust constrains this suggestion.

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#### A multi-isotope study for intrusion processes of mantle-derived melts in the lower crust: the case of the Tonian Goias stratiform complex

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Keywords: Layered Complex, Zircon, Isotope.

The Tonian Goiás Stratiform Complex (TGSC, Goiás, central Brazil), is one of the largest mafic-ultramafic layered complexes in the world, emplaced during the geotectonic events that led to the Gondwana accretion. We present trace elements and in-situ U/Pb - Lu-Hf analyses of zircons and <sup>87</sup>Sr/<sup>86</sup>Sr ratios of plagioclases from anorthosites and gabbros of the TGSC to investigate the processes that have controlled the intrusion of this huge volume of mantle-derived melts in the lower crust.

Although formed by three isolated bodies (Cana Brava, Niquelândia and Barro Alto), and characterized by a Lower and an Upper Sequence (LS and US), our new U/Pb zircon data confirm recent geochemical, geochronological, and structural evidences that the TGSC has originated from a single intrusive body, long ca. 350 km and thick ca. 20 km, in the Neoproterozoic.

New isotopic ratios reveal a complex contamination history for the TGSC, with different geochemical signatures in the two sequences. The low Hf and high Sr isotope ratios of the Lower Sequence suggest the presence of a crustal component and are consistent with contamination from meta-pelitic and calc-silicate rocks found as xenoliths within the Sequence. The more radiogenic Hf isotope ratios and low Sr isotope composition of the Upper Sequence suggest a contamination from mantle-derived metabasalts in agreement with the occurrences of amphibolite xenoliths in the US stratigraphy. The differential contamination of the two sequences is explained by the intrusion of the TGSC parental melt in a stratified crust dominated by metasedimentary rocks in its deeper part and metavolcanics at shallower levels. Moreover, the differential thermal gradient in the two crystallizing sequences might have contributed to the preservation and recrystallization of inherited zircon grains in the US and total dissolution or magmatic overgrowth of the LS zircons via melt/rock reactions processes.

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### Multiphase solid inclusions in the Ulten Zone peridotites: tracer of post-peak multi-stage crustal metasomatism in mantle wedge

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Keywords: multiphase solid inclusions, metasomatism, mantle wedge.

Multi-phase solid inclusions (MS) are an association of mineral inclusions hosted in a porphyroblast mineral (i.e. garnet). They are commonly considered to represent the crystallization products of trapped fluid and/or the results of fluid-mineral reactions (Frezzotti & Ferrando, 2007), thus providing information about the chemical composition of metasomatic fluids. This contribution deals with MS in a garnet-peridotite from the Variscan Ulten Zone (Eastern Alps, Italy), belonging to a metasomatized ultramafic body enclosed in gneisses and migmatites (Scambelluri et al., 2010). The studied rock shows a fine-grained amphibole-olivine-orthopyroxene-spinel-clinopyroxene matrix with an extensively fractured garnet porphyroclast surrounded by a kelyphitic corona. Garnet hosts randomly distributed spinel- and amphibole-bearing MS (where spinel and amphibole are the main minerals). The former consists of high-Cr spinel surrounded by Mg-horneblende, locally associated with dolomite and kinoshitalite (i.e. a Ba-rich phlogopite). In the latter Mg-horneblende, locally surrounding tschermakite, is associated with dissakisite (an REE-bearing epidote; Tumiati et al., 2005), apatite, dolomite, calcite, spinel, sapphirine, chlorite, kinoshitalite, and sulfides. Some reaction textures can be observed (i.e. sapphirine replacing low-Cr spinel, chlorite + kinoshitalite + tremolitic hornblende replacing Mg-horneblende.

Textural-chemical analyses and geothermobarometric calculations of MS can be used as an efficient tool to reconstruct the temporal sequence of metasomatic events. In particular, (major and some trace) elements partitioning between amphibole and other minerals helped to unravel the multimetasomatic history. Furthermore, the different composition between matrix amphibole and MS amphibole supports the hypothesis that MS are the result of garnet-fluid interaction rather than matrix minerals entrapped into garnet. During exhumation crustal-derived REE- and LILE-rich fluids infiltrated into the porphyroclast cracks and reacted with garnet generating peculiar mineral inclusion assemblages near peak conditions ( $\approx 850$  °C) and below 800 °C.

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Tumiati, S., Godard, G., Martin, S., Nimis, P., Mair, V. & Boyer, B. (2005): Dissakisite-(La) from the Ulten zone peridotite (Italian Eastern Alps): A new end-member of the epidote group. Am. Mineral., 90, 1177-1185.

## Fault-controlled hydrothermal flow over a deep magmatic intrusion inferred by numerical modelling in a back-arc tectonic setting, SE Tyrrhenian Sea

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Keywords: fluid circulation, PSDM, tectonics.

Hydrothermal flow over a magmatic system is one of the main-explored topic by scientific community during the last decades. Here we analyze hydrothermal circulation above a deep magmatic structure located offshore Capo Vaticano promontory (western Calabria coast). The magmatic intrusion may be related to melt migration from a deeper melting region above the Ionian subducting plate. In order to explain observations, we combine geophysical data and numerical modelling.

2D Fluid flow modelling was performed by using the Computational Fluid Dynamics (CFD) software (ANSYS FLUENT), that uses as input: 1) a geological section of the area, from interpretation of a pre-stack depth migrated multichannel seismic profile. The selected seismic line crosses the structural high in front of Capo Vaticano promontory above the magmatic intrusion; and 2) the temperature and heat flow conditions at the boundaries of the model. Model results highlight that temperature and geothermal gradient are mainly controlled by fluid flow pattern, which in turn is affected by fault distribution, by rock permeability, by basement topography and sediment thickness. Depth distribution of hypocenters of instrumental earthquakes, recorded since 2000 (http://cnt.rm.ingv.it/iside) within the active Tyrrhenian back-arc basin, suggests a depth of subducting plate greater than 70 km beneath our study area. A sufficient depth to allow partial melting of the mantle above the slab. Melt migration through the mantle wedge at shallower level forms the magmatic intrusion inferred by magnetic anomalies. The Pliocene Western Offshore Fault (Pepe et al., 2013) and the currently active Ridge 1 Fault (Loreto et al., 2015a), intensely fracturing the continental crust, enhance deep hydrothermal circulation. This hypothesis agrees well with documented observations (Loreto et al., 2015b) and represents a step forward in the knowledge of the Apennine subduction system. Furthermore, it adds new data to the tectonic framework of the inner Calabrian Arc dissected by numerous seismogenic normal faults capable to trigger highly destructive earthquakes.

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Loreto, M.F., Italiano, F., Deponte, D., Facchin, L. & Zgur, F. (2015b): Mantle degassing on a near shore volcano, SE Tyrrhenian Sea. Terra Nova, 27(3), 195-205.

Pepe, F., Bertotti, G., Ferranti, L., Sacchi, M., Collura, A. M., Passaro, S., & Sulli, A. (2014): Pattern and rate of post-20 ka vertical tectonic motion around the Capo Vaticano Promontory (W Calabria, Italy) based on offshore geomorphological indicators. Quat. Intern., 332, 85-98.

#### Mantle potential temperature of CFB in central Gondwana: Insights on lithosphere versus asthenosphere contributions

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Keywords: CFB, lithosphere-asthenosphere, Gondwana.

In this contribution, we present a comprehensive review of literature data (~2600 analyses), including major and trace elements and Sr-Nd isotopes, on continental flood basalts from the Ethiopia-Yemen, Deccan (India), and Karoo (southern Africa) volcanic provinces in order to evaluate whether they can be attributable to similar tectonomagmatic processes that occurred during the past 200 m.y. in central Gondwana. Results indicate that the three investigated provinces share fundamental features, such as the following: (1) Major and trace element compositions are closely comparable, in terms of parental magmas and fractionation trends, for the various continental fl ood basalt suites recognized in the provinces, namely, low Ti (LT, TiO, 0.5-3 wt%), high Ti (HT1, TiO, 1-4 wt%), and very high Ti (HT2, TiO, 2.5-7 wt%). (2) There is a clear zonal arrangement of continental fl ood basalts, with the hottest (potential temperature  $T_p$  up to ~1600 °C) and deepest (up to 5 GPa) HT picrite-basalt magmas in the central area and cooler and shallower LT basalts (T<sub>n</sub> down to 1450 °C, pressure [P] = 2-3 GPa) at the periphery, corresponding to a maximum thermal difference of 60-110 °C from the inner to the outer zones in each province. This conforms to continental flood basalt generation from a lenticular melting region, plausibly reflecting thermo-compositionally zoned plume heads, with maximum excess temperature  $T_{ex}$  = 250-300 °C with respect to the notional mid-ocean-ridge basalt (MORB) ambient mantle. (3) The central area of all provinces is characterized by the nearly exclusive occurrence of superheated HT picrite-basalt at the intersection of multiple extensional lineaments (faulting, rifting, and dike swarms), reflecting the focus of the tectonomagmatic activities. (4) The common occurrence of rhyolitic differentiates at the top of picrite-basalt lavas (e.g., Lalibela suite, northern Ethiopia; Pavagadh suite, Deccan; Lebombo suite, African Karoo). has to be considered an effect of the inversion of the stress regime, from generalized regional extension (continental flood basalt eruption) to localized continental rifting accompanying magma differentiation to rhyolites; Overall, results from this review provide compelling evidence that hot mantle plumes impinged diachronously on the central Gondwana lithosphere, causing similar tectonomagmatic events and continental flood basalt zonal arrangements that reflect a common thermocompositional zonation of the plume head in the three investigated provinces.

## The role of magmatism in the tectonic vs. climatic control on the Cenozoic evolution of the Earth's surface: a key to the "chicken or egg" conundrum?

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Keywords: Magmatism, Climate, Cenozoic.

Much of the research on feedbacks between mountain building, erosion and climate changes over geological timescales stems from the suggestion that uplift of Tibet triggered the Cenozoic climate cooling and the inverse proposal that climate cooling was responsible for inferred increases in mountain elevation and erosion. If climate cooling may explain widespread observations of a post ~5 Ma increase in global sedimentation/ erosion rates, weathering of fresh silicate minerals exposed at the surface through uplift and erosion consumes atmospheric  $CO_2$ , implying that enhanced denudation should be the cause, rather than the effect, of climate cooling. Long-term proxies of past atmospheric  $CO_2$  provide no clear evidence for the expected reduction in atmospheric  $CO_2$  concentrations in the late-Cenozoic, which led several authors to question the apparent increase in sedimentation and erosion rates.

Until now, this debate has paid little to no attention to the possible role of magmatic activity. However, on timescales of millions of years, magmatism directly impacts global climate through emissions of  $CO_2$  into the atmosphere and oceans, thereby buffering  $CO_2$  consumption by silicate mineral weathering. In turn, climate, tectonic and erosional changes control the distribution of the surface water, ice and rock masses, which can all affect magmatism by modulating the production, transfer and eruption of magma and hence the emissions of greenhouse gasses.

In this talk, I will present and discuss examples of geological contexts and events where the links between surface processes and magmatism appear particularly relevant and revisit the debate about the tectonic vs. climate control on the evolution of the Earth's surface in the light of these links. The objective is to explore the potential crucial role of magmatism in the coupled climatic, tectonic and erosional history of the Earth and stimulate research in this novel direction.

#### Lower crustal magma differentiation in continental setting: an example from the Layered Internal Zone in the Finero Mafic Complex (Ivrea Verbano Zone)

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Keywords: Lower crust, magma differentiation, Ivrea Verbano Zone.

Several evidences suggest that melt-rock reaction processes into the lower crust have an important role in the geochemical diversity recorded both in the mid-ocean ridge basalts (e.g. Lissenberg & Dick, 2008) and in the arc magmas (e.g. Smith, 2014). A strong effect of such processes even on the magmatism developed in continental settings is thus expected. Nevertheless, the geochemical signature of lower crustal differentiation is difficult to identify in continental setting because it is dominated and partially masked by shallow level differentiation processes.

The lower crustal sections exposed in orogenic settings are a unique opportunity to increase our knowledge on the magma differentiation processes in the lower continental crust. In this frame, the Finero Mafic Complex in the Ivrea Verbano Zone, representing an uplifted part of the pre-Alpine lower continental crust, is a natural laboratory. The Finero Mafic Complex consists of three different units (Siena and Coltorti, 1989): i) the Layered Internal Zone in contact with the mantle Phlogopite Peridotite; ii) the Amphibole Peridotite and iii) the External Gabbro. Here we focused on the Layered Internal Zone which is the deepest part of the mafic complex. We considered a relatively condensed section (about 1.5 m wide) consisting of a not cyclic alternation of gabbros, pyroxenites, websterites, peridotites, anorthosites and hornblendites layers. Fifteen samples representative of each lithology and of transition zones were investigated. Major minerals (olivine, pyroxenes, amphibole, garnet and plagioclase) were characterized through the transect for major and trace element composition by electron microprobe and laser ablation ICP-MS, respectively.

Chemical variations suggest that the pronounced lithological heterogeneity of the investigated transect is the product of at least two distinct magmatic events. In particular, preliminary data evidence that a preexisting association constituted by anorthosites, lherzolites, dunites, websterites and pyroxenites was intruded by a melt rich in  $H_2O$  and  $Al_2O_3$ . The gabbroic rocks and hornblendites formed as a result of the local reaction of such melt with different, preexisting cumulitic rocks. This work is a step forward in a better understanding of melt differentiation and migration processes in the lower crust.

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Siena, F. & Coltorti, M. (1989): The petrogenesis of a hydrated mafic-ultramafic complex and the role of amphibole fractionation at Finero (Italian Western Alps). Neues Jahrbuch für Mineralogie 6, 255-274.

Smith D.J. (2014): Clinopyroxene precursors to amphibole sponge in arc crust. Nature Communications 5, 4329

### Session S19 Melt/fluid-rock interaction and migration from the mantle to the surface

Conveners And Chairpersons Giulio Borghini (Università di Milano) Martina Casalini (Università di Firenze) Tommaso Giovanardi (Università di Modena e Reggio Emilia) Barbara Faccini (Università di Ferrara) Sciarra Alessandra (INGV, Roma)

# Subduction-related hybridization of the lithospheric mantle in mantle xenoliths from Tallante (Betic Cordillera, Spain)

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Keywords: Mantle xenoliths, in situ major and trace element contents, Sr-Nd-Pb isotopes.

Deep seated ultramafic xenoliths provide clues on the nature of the upper mantle giving insight on the nature and composition of sub-continental lithosphere; yet, they are rarely found at convergent plate margins. A notable exception is represented by the Betic Cordillera of southern Spain where the eruption of xenolith-bearing alkaline basalts during Pliocene post-dated the Cenozoic phase of plate convergence and subduction-related magmatism.

In this region the mantle xenoliths, hosted by a pyroclastic deposit of the monogenetic volcano of Tallante, display extreme compositional heterogeneities, plausibly related to multiple tectono-magmatic episodes that affected the area. Mantle xenoliths from Tallante show the occurrence of metasomatised veins of different size and mineralogy witnessing peculiar styles of metasomatism, which induces the crystallisation of quartz (qtz), orthopyroxene (opx), plagioclase (plg), phlogopite (phl), and amphibole (amph), beside the occurrence of several exotic accessory minerals such as apatite, thorite, huttonite, rutile, zircon and graphite. The metasomatic reactions produced different mantle metasomes characterised by "hydrous" opx-rich peridotite, locally crosscut by felsic veinlets. This indicates that the causative agents were hydrous silica-oversaturated melts rich in alkalis, plausibly related to the recycling - via subduction - of continental crust components within the mantle. The present study reports new evidence of suprasubduction metasomatic processes through new detailed major and trace elements and Sr-Nd-Pb analyses of the constituent minerals of composite Tallante xenoliths crosscut by centimetric felsic veins, in order to clarify the mode in which subduction related components are transferred to the mantle wedge in orogenic areas. The final goal is to provide new insights for the genesis of mafic alkaline potassic to ultrapotassic magmas in post-collisional tectonic settings

### Origin and melt-rock interaction history of the Mt.Maggiore pyroxenites (Corsica, France): Structural and geochemical insights

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Keywords: Alpine-Apennine ophiolites, Pyroxenite layers, Depleted peridotites.

Pyroxenite layers are minor but diffuse lithotype in fertile mantle peridotites and are considered an important component in the mantle source of oceanic basalts. Their origin may involve different processes, e.g. recycling of old oceanic crust, deep-seated melt intrusion and fractionation, reactive melt percolation at depth. Pyroxenites are rarely documented in abyssal and ophiolitic peridotites representing residual mantle after melt generation, and few studies defining their origin are to date available. We present microstructural and geochemical investigations of the pyroxenite layers in the depleted peridotites from the Mt.Maggiore ultramafic body (Alpine Corsica, France). Field relationships indicate that pyroxenites (mostly spinel websterites) occur as parallel layers preserving the same orientation throughout the whole peridotite massif. In places, they are affected and partly dissolved by the reactive melt percolation previously described in the associated peridotites. Clinopyroxene and orthopyroxene are partly replaced by interstitial olivine during spinel-facies reactive melt migration, and such olivine-rich "reactive pyroxenites" locally show plagioclase enrichment and [orthopyroxene + plagioclase] intergrowths crystallized at the expense of olivine and clinopyroxene, similar to what was described in the host spinel and plagioclase peridotites. Field and petrographic evidence thus indicates the formation of the pyroxenite layers prior to the multi-stage (spinel- to plagioclase-facies) meltrock interaction history related to progressive uplift of the peridotite body, in response to lithosphere extension and thinning. In the pyroxenites, both pyroxenes preserve high Al<sub>2</sub>O<sub>2</sub> contents up to 4.9 wt% in orthopyroxene and 7.2 wt% in clinopyroxene, similar to abyssal pyroxenites from slow- to ultraslow-spreading ridges (Dantas et al., 2007), and indicative of high-pressure crystallization (> 0.7 GPa). Geothermometric estimates on orthopyroxene-clinopyroxene pairs prior to exsolution (using areal analyses as representative of the primary pyroxene composition) yield high equilibrium temperatures (1220-1270°C). Preliminary in-situ trace elements data on clinopyroxenes have highlighted their depleted signature, characterized by significant LREE depletion  $(Ce_N/Yb_N = 0.005-0.03; Ce_N/Sm_N = 0.01-0.05)$ , similar to clinopyroxene in the host peridotites, as well as in abyssal pyroxenites (e.g. Dantas et al., 2007). Further investigations are needed to understand whether such compositions reflect a depleted signature of parental melts, or they are related to the melting and melt-rock reaction processes that affected the associated peridotites.

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#### Melt inclusions in (U)HP garnet clinopyroxenite and eclogite of the Bohemian Massif

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Keywords: pyroxenite, orogenic peridotite, eclogite.

Melt inclusions have been identified in garnet clinopyroxenites of the Granulitgebirge and in UHP eclogite of the Erzgebirge, Bohemian Massif. This discovery allows the direct investigation of the deep melts generated during continent-continent collision.

In the Granulitgebirge the garnet clinopyroxenite occur as single layers enclosed in orogenic peridotite. The inclusions, 5-20 µm in diameter, are both glassy and polycrystalline, i.e. nanogranitoids, and they occur in clusters in the inner part of the garnet. The mineral assemblage in the nanogranitoids consists of has been and is kumdykolite/albite, phlogopite, osumilite, kokchetavite and quartz, identified via Raman spectroscopy and EDS mapping. Microstructural and microchemical features suggest that they were former droplets of melt trapped while the garnet was growing as a peritectic phase along with clinopyroxene. As a consequence the melt is likely to be genetically connected with the formation of the whole pyroxenite body. We re-homogenized the nanogranitoids using a piston cylinder apparatus at 1000-1050 ° C and 22-15 kbar, conditions expected for the garnet formation and thus of the melt entrapment. The melt is hydrous, trondhjemitic to granitic in composition and enriched incompatible elements such as Cs, Rb, Ba, Pb, Li and B and with negative anomalies in Nb, Ta and Sr. The patterns suggest the involvement of the phengite/white mica, i.e. a crustal component, in the melting producing reaction. This crust-mantle interaction may be the result of two possible processes: (1) localized partial melting of a phengite-bearing rock with the simultaneous production of melt, garnet and clinopyroxene or (2) infiltration of an external melt which interacts metasomatically with the peridotite generating the whole pyroxenite.

In the Erzgebirge case study, the UHP eclogite occur in lenses and blocks in diamond-bearing gneisses. Preliminary investigation shows that these inclusions, 5-25 µm in diameter, range from polycrystalline to glass and occur as clusters in the inner part of the garnet. The mineral assemblage is biotite, quartz/rare cristobalite, white mica, kumdykolite or (more rarely) albite, and carbonate with variable amounts of kokchetavite and graphite. Further investigation on the melt geochemistry will improve our understanding of the crustal melting processes at mantle depths and, in general, will provide new constraints for melt-rock interaction and partial melting processes involving mafic/ultramafic rocks in collisionl setting.

#### Pyroxenite-peridotite interactions in upwelling veined mantle: an experimental study at 2 GPa

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Keywords: pyroxenite, peridotite, melt-rock reaction.

Melts produced by partial melting of pyroxenite within an upwelling mantle are expected to react with the surrounding peridotite likely creating hybrid rocks (i.e. refertilized peridotites and secondary-type pyroxenites). The resulting veined mantle has been diffusely invoked as a suitable source of oceanic basalts (e.g. Lambart et al., 2012). We experimentally investigated the reaction between a fertile lherzolite and partial melts produced by a mantle pyroxenite at 2 GPa. Melting behavior of garnet websterite Px-1 (e.g. Sobolev et al., 2007) has been firstly derived. Px-1 starts to melt just below 1280°C, and up to 1350°C it produces MgO-rich basaltic andesites. Garnet and clinopyroxene are progressively consumed by melting (at 1330 and 1380°C, respectively); orthopyroxene is the liquidus phase and is completely exhausted at 1400°C.

We carry out piston cylinder reaction experiments by juxtaposing pyroxenite Px-1 on a powdered fertile lherzolite, previously synthesized at the same P-T conditions of reaction experiments. This allows a direct comparison between the modal and mineral compositions in the fertile lherzolite and in the peridotite modified after reaction with pyroxenite-derived melt. At 1300 and 1350°C, partially molten pyroxenite interacts with the subsolidus lherzolite producing a thin (about 50-100 µm) orthopyroxene-rich reaction zone at the pyroxeniteperidotite interface. Chemical profiles along the capsules show that X<sub>Mg</sub> and Cr<sub>2</sub>O<sub>3</sub> content in pyroxenes decreases, and TiO, increases, across the pyroxenite-peridotite boundary, with intermediate values in the reaction zone. At 1300°C, residual pyroxenite is more depleted in Fe than after partial melting alone, at the same temperature, and this inhibits the stability of residual garnet. Remarkably, in the subsolidus lherzolite spinel records  $X_{Mg}$  and  $X_{Cr}$  decrease and TiO<sub>2</sub> increase going toward the molten pyroxenite, with spinel  $X_{Cr}$ variation increasing with temperature. Similar chemical gradients are observed in some natural pyroxeniteperidotite sequences. Experimental results suggest that element diffusion across the two starting layers is able to modify mineral chemistry of subsolidus peridotite. At 1380°C, interaction between pyroxenite-derived melt and low-degree molten peridotite resulted in a larger orthopyroxene-rich layer (about 650 µm), also containing few low-Ca clinopyroxene and glass-bearing tasks. Remarkably, relatively high-TiO, content in clinopyroxene and low X<sub>cr</sub> spinel suggest that pyroxenite-derived melt percolated into the peridotite layer likely profiting of porosity created by low-degree of peridotite partial melting.

Lambart, S., Laporte, D., Provost, A. & Schiano, P. (2012): Fate of pyroxenite-derived melts in the peridotitic mantle: thermodynamic and experimental constraints. J. Petrol., 53, 451-476.

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#### Chemical modification of mantle peridotite via interaction with pyroxenite-derived melt in Northern Apennine ophiolites (Italy)

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Keywords: melt-rock reaction, pyroxenite, mantle heterogeneity.

Pyroxenites are crucial components in mantle melting and the interaction of pyroxenite-derived melts with surrounding peridotite leads to significant chemical modification of the mantle source of basalts (e.g. Lambart et al., 2012). Metasomatic effects of melts percolating through a mantle column have been widely documented. However, few studies focused on orogenic peridotites locally modified by associated pyroxenites. Pyroxeniteperidotite mantle sequences of External Liguride Units (Northern Apennines, Italy) represent a proxy of veined MORB mantle (Borghini et al., 2013). They preserved the chemical variability inherited from deep melt infiltration representing an excellent study case to investigate how pyroxenite emplacement modifies the chemical composition of the MORB mantle. Pyroxenites occur as cm-thick layers parallel to mantle tectonite foliation. They are websterites and clinopyroxenites originated from melt segregation at rather high pressures (P > 1.6 GPa). Diffuse orthopyroxene-rich layers along the pyroxenite-peridotite contact indicate a relatively high silica activity of pyroxenite parental melts, also having relatively low  $X_{Mg} [X_{Mg} = Mg/(Mg+Fe) < 62]$ , possibly derived from a mafic rock-bearing mantle source (Borghini et al., 2016). We performed centimeterscale profiles across the pyroxenite-peridotite boundary in which the wall-rock peridotite is up to 4 cm from the pyroxenite, host peridotite from 4 to 25 cm from the pyroxenite, and country peridotite, more than 2 m from pyroxenite layers. Relative to country peridotites, wall-rock peridotites show i) modal orthopyroxene enrichment at the expense of olivine, ii) higher Al, Ca, Si contents and slightly lower X<sub>Me</sub>, iii) Al-richer spinel and lower-X<sub>Mg</sub> pyroxenes. Along the pyroxenite-peridotite traverses, clinopyroxenes record a trace element gradient: at the pyroxenite-peridotite contact they have the lowest MREE-HREE abundances, and overall REE contents progressively increase away from the pyroxenite up to about 20 cm. Beyond 20 cm, the HREE content decreases while the LREEs remain at nearly constant level. We modeled the trace element gradient in clinopyroxene by numerical simulation of reactive melt percolation from pyroxenite through the host peridotite using Plate Model (Vernieres et al., 1997). Assuming olivine assimilation combined with orthopyroxene and clinopyroxene precipitation, model results indicate that percolative reactive flow at decreasing melt mass and rather high instantaneous melt/peridotite ratio (initial porosity of 10%) accounts for the overall REE enrichment in the first 20 centimeters of peridotite. Farer, the progressively reduced mass of the percolating melt, possibly in presence of increasing crystallization rates, causes a more efficient chemical buffering of the host peridotite on the HREE composition of the differentiated liquids through ion exchange chromatographic-type processes, determining the observed increase of the LREE/HREE ratio.

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## Lithosphere evolution beneath the Adria Plate: Re-Os systematics of sulfides in mantle xenoliths from Veneto Volcanic Province (North-East Italy)

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Keywords: Re-Os, sulfides, craton.

The Veneto Volcanic Province (VVP) is one of the widest Cenozoic magmatic districts of the Adria plate. From late Paleocene to early Miocene, the VVP magmatic activity formed the volcanic districts of Val d'Adige, Lessini Mts, Marosticano, Berici Hills, and Euganean Hills. According to literature, magma formation appears to have been triggered by decompression related to the extensional deformation in the South-alpine foreland during the Alpine orogenesis. Most of the volcanic products are relatively undifferentiated lavas, from nephelinites to tholeiites and commonly carry mantle xenoliths. According to previous studies on Val d'Adige and Lessini Mts peridotites, the mantle beneath the VVP exhibits geochemical features typical of off-craton mantle variably affected by Na-alkaline silicate metasomatism (Beccaluva et al., 2001). However, a newly discovered suite of anhydrous, spinel-bearing mantle peridotites from the Marosticano district exhibit (i) highly refractory compositions comparable with those observed for cratonic peridotites worldwide and (ii) clinopyroxene major and trace element compositions consistent with carbonatite/CO2-rich silicate metasomatism. To test the cratonic signature of the Marosticano mantle domain Re-Os in-situ measurements on sulfides and alloys were performed for the first time on VVP mantle domain. The Re-Os model ages  $(T_{MA})$  range between 1.8 and 2.8 Ga, with a value at  $3.1 \pm 0.08$  Ga, confirming the derivation of Marosticano peridotites from ancient mantle and also suggesting a "hidden" cratonic signature for Val d'Adige and Lessini Mts lithospheric mantle. These results allow a re-interpretation of the geodynamic evolution of the VVP lithosphere. The Marosticano domain can be interpreted as a vestige of an Archean/Proterozoic cratonic domain, whose signature was not erased by the carbonatite/CO<sub>2</sub>-rich silicate metasomatism, whereas the xenoliths from the Lessini Mts and Val d'Adige are remnants of circumcratonic domains compositionally rejuvenated by infiltration of asthenospherederived melts. According to González-Jiménez et al. (2013), the VVP Re-Os data enlarge the Archean domain previously recognised within the Alpine domain in the Central Mediterranean area, in contrast with the younger age revealed in the European and African lithosphere.

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#### The storing capabilities of the upper mantle/lower crust for As and Sb: insights from experimental studies

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Keywords: As and Sb, experiment, lower crust.

The chemical heterogeneity of the Earth's mantle is the result of the interaction of melt production and melt migration. The knowledge of trace elements partitioning in key mantle minerals and melt is fundamental to understand how the different elements migrate in the mantle and which mechanisms drive mantle refertilization. Recently, As and Sb has been recognized as important elements to track fluid-mediated mass transfer at depth. However, their partitioning in major mantle minerals and melt is still poorly constrained. Olivine and pyroxene represent the most abundant mineral phases in the upper mantle/lower crust. However, in fluid-bearing systems amphibole, with its versatile crystal structure, might significantly contribute in the trace element budget.

In order to better constrain the partitioning of As and Sb among major mantle minerals and melt we performed high pressure experiments at 1.4 GPa starting from an alkali-basalt doped with a series of petrologically relevant trace elements. As and Sb have multiple oxidation states that may influence the solid/melt partitioning; for this reason experiments were carried out both at hematite-magnetite buffer ( $\approx$ FMQ+1.7), and using a graphite inner capsule to maintain the oxygen fugacity ( $fO_2$ ) close to the CCO buffer ( $\approx$ FMQ-2.5). Experiments were performed at fluid saturation conditions, heated up to 1300°C, and slowly cooled down to the experimental temperature (from 1075 to 1015°C) and then quenched. Run products were characterized for major element composition by EMPA and for As and Sb concentrations by LA-ICP-MS.

At higher oxygen fugacity and temperature (1075°C) glass + clinopyroxene (Mg# 0.72)  $\pm$  mica  $\pm$  titanite is the stable assemblage. At lower temperature (1050-1015°C) amphibole (pargasite/kaersutiite) crystallizes replacing clinopyroxene (Mg# 0.74-0.77). At lower oxygen fugacity amphibole start crystallizing at 1040°C replacing clinopyroxene thus suggesting that redox conditions do not significantly affect the mineral assemblage and the thermal amphibole stability field.

At lower  $fO_2$  conditions As and Sb concentrations are extremely lower in clinopyroxene and amphibole relative to the equilibrium melt, thus showing a highly incompatible behavior. Data at higher  $fO_2$  suggests that As and Sb increase their compatibility for amphibole. However, mass balance calculation have shown that a significant loss of As and Sb in the system has occurred due to their affinity with Pt capsule. We are currently evaluating if the loss of As and Sb may have affected the calculation of the <sup>S/L</sup>D.

Our preliminary results suggest that at low  $fO_2$  conditions the upper mantle/lower crust do not store significant amounts of As and Sb. More suitable conditions to fix As and Sb in the upper mantle/lower crust seem to be at higher  $fO_2$  conditions.

## Wetting angles of hydrous carbonatitic liquids and reversal in wettability for silicate and carbonatitic magmas in the mantle

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Keywords: Mantle peridotite, Dihedral angle, COH species.

Carbon-bearing solids, fluids, and melts in the Earth's deep interior play an important role in the long-term carbon cycle. Carbonatite magmas have been suggested as important agents of mantle metasomatism and yet, their physical features are expected to control the mobility from the source region to shallow Earth. The mobility and infiltration rates of carbonatitic melts, together with their influence on the annealing of mantle peridotites are poorly constrained processes. Although natural carbonatitic melts are complex chemical systems with C-O-H species as a major component, previous work has been performed in anhydrous model systems. Here we present a quantitative laboratory simulation of variables and processes controlling the ascent, mobility and connectivity of carbonatites in a model mantle material investigating the dihedral angle of hydrous carbonatitic liquids. We aim at comparing the texturally equilibrated volume proportions of volatile-rich carbonatitic melts with silicate melts in a partially molten peridotite, and we examine whether carbonatitic liquids are always more wetting than silicate melts. The infiltration experiments were performed employing an end loaded pistoncylinder apparatus, at  $T = 1200^{\circ}$ C and P = 2.5 GPa to investigate the percolation of carbonatitic liquids and interconnectivity of melt pockets in a peridotitic matrix. Hydrous carbonatitic melt pockets were found along olivine grain boundaries; image analysis on electron back scattered and X-ray maps allow us quantifying the apparent dihedral angles between the liquid and olivine and to calculate the grain boundary wetness. Experiments performed at 5 wt.% of water contents result in dihedral angles evolving from  $\sim 31^{\circ}$  to  $\sim 41^{\circ}$  with a volume of liquids from 2 to 10 vol.%, while experiments carried out at 30wt. % of water content show a dihedral angle values of almost 50° with a range of volume infiltrated melts between 4 to 9 vol. %. These results indicate that dihedral angles progressively increase with increasing water dissolved from 25°-28° in anhydrous carbonatitic liquids up to 50° in water-rich carbonatitic liquids, and, as expected, the volume of interstitial liquid decreases with water increasing. The increase of wetting angles is representative of a sintering process of the solid matrix, which evolves with time in the development of channels of pores, as highlighted relating the grain boundary wetness with fraction of liquid infiltrated. We suggest that the low grain boundary wetness measured may be due to a relatively low melt-rock interfaces which develop with channelized liquid, and that channelization is promoted by chemical gradient, as established by a carbonatitic segregate in the silicate matrix. If H<sub>2</sub>O is available, we expect that H<sub>2</sub>O strongly partitions into carbonatitic liquids. As a result, their dihedral angle may evolve up to 50°, a value which is significantly higher than that characterizing silicate melts at similar mantle conditions.

#### Water content in nominally anhydrous minerals (NAMS) from subcontinental mantle bodies of the Ivrea-Verbano zone (southern Alps)

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Keywords: Nominally Anhydrous Minerals, Subcontinental Mantle, Ivrea-Verbano Zone.

One of the peculiarities of the Ivrea-Verbano Zone (IVZ, Southern Alps) is the presence of several mantle bodies, among which those famous of Finero, Balmuccia and Baldissero, within lower continental crustal rocks. Despite the numerous studies on these mantle lenses, the mechanisms and the geodynamic settings leading to their emplacement into the continental crust are still poorly-constrained, even though they are commonly attributed to collisional orogenic systems (Quick et al., 1995).

To place further constraints on the geodynamic evolution of subcontinental lithospheric mantle and of the IVZ sequence, a new investigation on the main mantle bodies is ongoing, by combining the study of the water content in hydroxyl forms (OH) detectable by means of infra-red spectroscopy (FTIR) in the Nominally Anhydrous Minerals (NAMs) to conventional field, petrographic and geochemical surveys.

Hydrogen is present only as a trace element in NAMs composing the Earth's mantle, but its abundance is believed to have important consequences on fundamental physical properties such as rheology, seismic attenuation and electrical conductivity (Padròn-Navarta et al., 2017). Although there is a wide literature on hydrogen distribution in NAMs from relatively dry mantle xenoliths, there is a remarkable absence of data on Alpine orogenic peridotites. The current investigation aims at filling such a gap and providing important information about the petrological evolution of the mantle sequences, in particular as a consequence of melt-related processes, and the rheologic and physical properties of subcontinental mantle rocks.

Preliminary data for the Finero Phlogopite Peridotite show that i) the olivine water content is around 2 ppm, with only minor variations depending on the lithology and texture and ii) the water contents in orthopyroxene and clinopyroxene are also comparatively low (around 42 and 137 ppm, respectively). These values are surprisingly low considering the water-rich nature of the Finero Phlogopite Peridotite, which experienced K-rich metasomatism documented by pervasive crystallization of hydrous mineral phases, such as amphibole and phlogopite (up to 25 vol. %).

In order to better understand the role of i) bulk rock and mineral composition and ii) the occurrence of hydrous minerals on the OH budget, the water content in NAMs data have been acquired for the Balmuccia and Baldissero mantle bodies, which are conversely characterised by weak to absent metasomatism and considered representative of DM lherzolitic reservoir.

Quick, J.E., Sinigoi, S. & Mayer, A. (1995): Emplacement of mantle peridotite in the lower continental crust, Ivrea-Verbano Zone, northern Italy. Geology, 23, pp. 739-742.

Padròn-Navarta, J.A. & Hermann, J. (2017): A subsolidus olivine water solubility equation for the Earth's upper mantle. JGR, 122, 9862-9880.

### Morb-type gabbros emplacement during the Red-Sea continental break-up: a case study from the Tihama Asir magmatic complex

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Keywords: Morb-type gabbros, Red-Sea continental break-up, Tihama Asir magmatic complex.

The nature of the lithosphere forming the ocean-continent transitions is still highly debated. Recent evidence on hyper-extended margins attests that in magma-poor systems a newly formed oceanic crust may occurs as discrete plutons intruded within exposed subcontinental mantle rocks, whereas volcanics and dyke complexes are locally absent. On the other hand, it has been argued that at higher magma production rates gabbros can be emplaced within the lower continental crust, leading to the final phases of continental breakup and opening of an oceanic basin. Here we report new data from a gabbroic intrusion located in the southernmost region of Saudi Arabia, within a magmatic system called Tihama Asir complex (McGuire and Coleman, 1986). Previous K-Ar determinations on these gabbros constrain the age of formation at 20 to 24 Ma (Coleman et al. 1979), coeval with the opening of the Red Sea basin at these latitudes. New major and trace element determinations on bulk rock and on mineral phases allow us constraining the geochemical fingerprint of the melts that formed these intrusions. We distinguish two different typologies of gabbroic rocks, coexisting in the Tihama Asir complex. The first typology is represented by layered olivine gabbros to anisotropic olivine-free gabbros, having a mineralogical and geochemical composition undistinguishable to those of abyssal gabbros forming the modern lower oceanic crust. On the other hand, the second typology is constituted by oxide-bearing to oxide-enriched gabbros locally having a peculiar porphyritic texure, and a enriched incompatible trace element signature. We interpreted this second gabbro typology to be formed by a interaction between a cumulate and a melt that suffered a certain degree of contamination from continental material. If corroborated by isotopic data, our preliminary results sustain the idea that the breakup of the Red Sea ocean was preceded by the injection of MORB-type melts derived from the asthenosphere into a thinned Arabian continental crust.

Coleman, R.G., Hadley, D.G., Fleck, R. J., Hedge, C.E. & Donato, M.M., (1979): Miocene Tihama Asir complex and its bearing on the opening of the Red Sea, in AL-SHANTI, A. M., ed., Evolution and Mineralization of the Arabian-Nubian Shield, Vol. 1, Oxford, Pergamon Press Ltd., p. 173-186.

McGuire, A.V. & Coleman R.G. (1986): The Jabal Tirf layered gabbro and associated rocks of the Tihama Asir Complex, SW Saudi Arabia, Journal of Geology; 1986, vol. 94, p. 651-665, University of Chicago.

### Tholeiitic refertilisation vs alkaline metasomatism within the Transylvania Basin mantle wedge

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Keywords: subduction, mantle xenoliths, refertilisation.

Pleistocene (1.2-0.7 Ma) volcanics of Perşani Mts was the last alkaline magmatic manifestation in the complex evolution of the Carpatho-Pannonian region, contemporaneous with the near South Hargita Pliocene-Quaternary calcalkaline eruptions. From late Miocene to Pliocene, the main driving force for the evolution of this area was the interplay between subduction slab rollback and back arc asthenospheric mantle uprise, this latter to compensate the instability caused by the gravitational sinking of high-density oceanic lithosphere.

Mantle xenoliths are abundantly found in the eruptive products of Perşani Mts, with textures varying from protogranular to porphyroclastic including several intermediate subtypes. The great majority are fertile spinel lherzolites (modal cpx and spinel up to 22 and 5.5 vol%, respectively) in which disseminated pargasite is associated with cpx and opx and, to a lesser extent, spinel. Few nodules also have amphibole veins.

Whole rock compositions show enrichments in basaltic components but not the initial enrichment in  $\text{FeO}_{tot}$  typical of low-degree partial melting between 1 and 3 GPa for fertile peridotites. As a consequence, their  $\text{Al}_2\text{O}_3$  content is higher than expected for the corresponding MgO predicted by the models.

Mineral chemistry testifies that all phases attained equilibrium. Particularly cpx1 exhibit a rather large range of mg# (89.0-92.9) and  $Al_2O_3$  contents (up to 8.16 wt%) higher than those expected for cpx1 in PM. Their REE patterns vary from slightly depleted to slightly enriched, perfectly mimicked by those of the associated disseminated amphiboles.

The possibility that cpx composition represents un-melted portion of a PM is unlikely. Their fertility can be explained only by a complete refertilization of a pristine mantle lithology. The metasomatic agent likely was a high  $Al_2O_3$  tholeiite with arc affinity, as testified by mass-balance reaction calculations and by the low Nb content of disseminated amphiboles.

Evidences that this melt/fluid was subduction-related are also inferred from the He-Ne-Ar systematics in FI. Mean  ${}^{3}\text{He}/{}^{4}\text{He}$  in ol, opx, and cpx (5.8 Ra) is well below MORB range (8±1 Ra) and comparable to other European magmatic provinces where subduction imprint is evident ( ${}^{3}\text{He}/{}^{4}\text{He} < 6$  Ra, Tallante; Martelli et al., 2011). In addition, Ne and Ar isotope ratios clearly indicate a strong air contamination that would occur already in the mantle due to volatiles recycling.

The last metasomatic event is testified by the vein amphiboles which have lower mg# and higher  $K_2O$ ,  $TiO_2$ , LREE and Nb contents than disseminated amphiboles. Their patterns approach those of the alkaline megacrysts found in the area and can be explained as the result of the interaction with an alkaline magma.

Martelli, M., Bianchini, G., Beccaluva, L. & Rizzo, A. (2011): Helium and argon isotopic compositions of mantle xenoliths from Tallante and Calatrava, Spain. J. Volcanol. Geotherm. Res. 200, 18-26. doi:10.1016/j.jvolgeores.2010.11.015.

#### Olivine-rich troctolites as a result of melt-dunite interactions: an experimental study

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Keywords: Melt-rock reactions, reactive crystallization, olivine-rich troctolites.

Studies on oceanic lithosphere suggested that melt-rock reactions play a key role in the origin of olivine-rich troctolites. In order to provide experimental constraints, we performed reactive dissolution and crystallization experiments by reacting variably evolved MORBs with pre-impregnated San Carlos olivine at 1300°C and then cooling to 1150°C at constant pressure (0.5 and 0.7 GPa). Additionally, an isothermal experiment (0.7 GPa, 1250°C) provides a snapshot of olivine-melt reaction after the high-temperature step. Although high-porosity trap has been used, only limited reactive melt percolation occurred. Runs result in glass-bearing gabbro overlain by olivine-rich troctolite/dunite showing disequilibrium textures comparable with natural occurrences typically related to melt-rock reaction, e.g. embayed and resorbed subhedral olivine with lobate contacts against plagioclase and clinopyroxene, often occurring as large poikiloblasts including rounded olivines. Textural and chemical observations on olivine-rich layer suggest that interactions occurred at rather low melt/olivine ratio. We found that higher pressure further limits the extent of olivine dissolution and results in a lower high-T porosity, decreasing the final abundance of interstitial phases. Olivine dissolution and re-precipitation combined with element diffusion reset the composition of starting olivine, by lowering its  $X_{M\sigma}$  and NiO content as a function of melt-olivine ratio. Regardless the basalt composition, olivine  $X_{M\sigma}$ approaches 0.88 Melt composition affects the chemistry of interstitial minerals, that show, mostly at high pressure large compositional variability (anorthite in plagioclase, TiO<sub>2</sub> in clinopyroxene) as a result of local equilibrium driven by trapped melt effect. Remarkably, mineral co-variation trends (e.g. plagioclase anorthite vs. olivine X<sub>Mg</sub>) match those of some natural olivine-rich troctolites settings, supporting the lead role of meltrock reactions in their origin.

### The Tortuga Hill mantle xenoliths (Central Patagonia, Argentina): evidence for variable depletion and metasomatism far away from the subduction zone

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Keywords: Mantle Xenoliths, Partial Melting, Metasomatism.

Cerro Tortuga is a volcanic neck located 600 km east from the Chile trench (San Jorge basin, Southern Chubut province) composed by Oligocene-Miocene basalts and gabbros. The basalts carry spinel-facies mantle xenoliths, providing insight in the mantle composition and processes.

The mantle column beneath Cerro Tortuga appears fertile as 12 out of 16 studied samples are anhydrous lherzolites, accompanied by subordinate Cpx-bearing harzburgites. They display porphyroclastic and mosaic-porphyroclastic textures in equal proportions. However, the degree of deformation is lower compared to mantle xenoliths from other central Patagonia localities (e.g. Paso de Indios): it resulted in a grain-size reduction of olivine, which locally shows kink-bands. Besides, many samples preserve rounded to stretched clusters made of large Sp and Opx±Cpx, commonly interpreted as the result of Gnt breakdown at spinel-facies condition. Estimated equilibrium temperatures based on Brey & Köhler (1990) and Nimis & Taylor (2010) geothermometers are in good agreement, in the range of 870-960°C and 830-940°C, respectively.

The xenoliths define an array in the Cpx/Opx vs. Cpx (Vol.%) diagram consistent with 1 to 25% partial melting of Primitive Mantle. The decrease in modal Cpx is associated with increasing Mg# in all the silicates and decreasing Al in spinel and pyroxenes, as expected after variable degrees of partial melting.

A derivation from partial melting is confirmed for the most fertile lherzolites (Cpx > 10 Vol.%) by the Cpx composition, which is depleted in LILE, Nb, Ta, Th, U and LREE, but enriched in HREE (> 10xCI). The overall REE fractionation is consistent with 4% fractional melting of Primitive Mantle. Conversely, Cpx from Cpx-poor lherzolites (Cpx < 10 Vol.%) and harzburgite show large Th, U, L-MREE and Sr contents pointing to metasomatic interaction with melts extremely enriched in highly incompatible elements. Some harzburgite Cpx have peculiar Zr and Hf enrichments, previously found in rare mantle xenoliths from volcanic arcs (El Fraile; Faccini et al. 2013) and alkaline pyroxenites (Raffone et al. 2009); this is the first evidence of such geochemical feature in the extra-Andean mantle.

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Faccini, B., Bonadiman, C., Coltorti, M., Grégoire, M. & Siena, F. (2013): Oceanic material recycled within the sub-Patagonian lithospheric mantle (Cerro del Fraile, Argentina). J. Pet., 54, 1211-1258.

Nimis, P. & Grütter, H. (2010): Internally consistent geothermometers for garnet peridotites and pyroxenites. Contrib. Mineral. Petrol., 159, 411-427.

Raffone, N., Chazot, G., Pin, C., Vannucci, R. & Zanetti, A. (2009): Metasomatism in the lithospheric mantle beneath Middle Atlas (Morocco) and the origin of Fe- and Mg-rich wehrlites. J. Pet., 50, 197-249.

#### Hydrogen distribution in plagioclase from the Atlantis Bank Gabbros (IODP hole u1473): preliminary data

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This contribution reports preliminary data on the H distribution in plagioclase from abyssal gabbros recently drilled from an oceanic core complex (Hole U1473A, SW Indian Ridge). Our project is aimed to reassess models for the rheology of the lower ocean crust by focussing on porphyroclastic and neoblastic plagioclase in plastically-deformed abyssal gabbros. Current models hold that the lower crust is fundamentally strong, consistent with dry-plagioclase flow laws. However, geochemical and structural evidence suggest that the crust can be fundamentally weak near-axis, controlled primarily by the behaviour of wet plagioclase in near-pervasive shear zone networks (MacLeod et al., 2017). A quantification of H in deformed gabbros is thereby fundamental to demonstrate the link between water and deformation in order to upscale the appropriate wet flow laws gaining a very different understanding of ocean crust rheology. We selected gabbroic samples at variable degree of deformation where shear zones were very probably wet under hyper-solidus to hightemperature sub-solidus (~granulite facies) conditions. FT-IR maps were acquired with a spot diameter from 100 to 30 µm<sup>2</sup> on plagioclase ranging from large porphyroclasts to neoblasts. Our preliminary FT-IR results undoubtedly show that H concentrations in plagioclase is extremely heterogeneous and in many cases clearly concentrated along fractures or grain boundaries. A preliminary knowledge of the distribution of H in "anhydrous" mineral is thereby fundamental to obtain a quantification of the water incorporated into the mineral lattice at high temperature, avoiding any effect related to low temperature alteration and/or subsolidus diffusion during cooling. When the contribution of this late-stage H enrichment in plagioclase is removed, our maps clearly show that the H contents increase within the shear zones. If confirmed, a link between water content and deformation intensity would allow to use the appropriate wet flow laws gaining a very different understanding of ocean crust rheology.

MacLeod, C.J., Dick, H.J.B., Blum, P. & the Expedition 360 Scientists (2016): Southwest Indian Ridge Lower Crust and Moho. Proceedings of the Integrated Ocean Drilling Program. Volume 360. DOI: 10.14379/iodp.pr.360.2016.

# The oxidation state of spinel-peridotites from the Hyblean plateau and the modeled composition of coexisting C-O-H fluids

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Keywords: ferric iron, carbon, Mössbauer.

The study of the oxidation state of Earth's interior is crucial for understanding the processes that govern the speciation of volatiles, in particular carbon that, depending on the local oxidation state, can occur as diamond/ graphite, carbonate minerals,  $CO_2$ -bearing melts or fluids coexisting along with the more abundant mantle silicates. This study focused on the determination of the oxidation state of spinel (spl) peridotites from the Hyblaean Plateau and the thermodynamic determination of potentially coexisting mantle fluids in the C-O-H chemical system.

We selected seven mantle xenoliths sampled in the Miocene diatreme of Valle Guffari (Catania). These rocks were classified as spl lherzolites and harzburgites, based on the abundance of coexisting olivine, orthopyroxene and clinopyroxene, and appear to be equilibrated at a pressure between 0.9 and 1.2 GPa and temperatures between 950 and 1050 °C.

The ferric iron content of spl was measured by conventional <sup>57</sup>Fe Mössbauer spectroscopy at the Department of Earth Sciences, Sapienza University of Rome, except few small grains that were measured using in situ Mössbauer spectroscopy at beamline ID18 of ESRF (Grenoble, France).

The Fe<sup>3+</sup>/ $\Sigma$ Fe ratio of spinel ranges between 27% and 30%. These data were used to estimate the oxygen fugacity of each xenolith employing two different oxy-barometers by Ballhaus et al. (1991) and Miller et al. (2016). Our results show that the Hyblaean mantle redox state varies from 0.4 log units to 1.6 log units with respect to fayalite-magnetite-quartz buffer used as reference, supporting, therefore, the possible coexistence of C-O-H fluids along with the equilibrated mantle minerals.

The chemical composition of the coexisting fluids for each sample was calculated using the Zhang and Duan (2009) thermodynamic model. Our calculations resulted in fluids consisting mainly of  $H_2O$  with up to 14 mole% of dissolved C. Results from this study show that spl peridotites from Valle Guffari record an oxidation state that does not allow the presence of graphite. Instead, it seems favorable to the stability of  $CO_2$ -bearing  $H_2O$ -rich fluids that may have led to onset of partial melting processes in depth.

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Miller W.G.R., Holland T.J.B. & Gibson S.A. (2016): Garnet and Spinel Oxybarometers: New Internally Consistent Multi-equilibria Models with Applications to the Oxidation State of the Lithospheric Mantle. Journal of Petrology, Vol. 57, No. 6, 1199-1222.

Zhang C. & Duan Z. (2009): A model for C-O-H fluid in the Earth's mantle. Geochimica et Cosmochimica Acta, 73(7), 2089-2102.

#### The Phlogopite-Bearing ultramafic rocks: a new proposal for their classification

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Keywords: Phlogopite, Ultramafic Rock, Modal composition.

In recent years, the many new occurrences reported in the literature of ultramafic rocks with phlogopite as a major constituent and not falling into the category of Kimberlites, Lamproites and Lamprophyres, have highlighted the need of a classification that includes this abundant mineral phase. Currently, a broadly accepted classification with phlogopite does not exist and the only term used by scientists is 'bearing phlogopite' in association with the current classification of ultramafics, thus not considering the % of phlogopite volume, which can vary from 5 % by Vol. up to 90 %. Moreover, some of the nomenclature used to describe this type of rocks is rather obsolete. For example, the term "Abessedite" indicates a variety of peridotite composed of olivine, hornblende and phlogopite, the name "Pikeite" denotes a phlogopite peridotite, or "Scyelite" that describes an olivine-hornblendite with phlogopite For this reason, we propose a new classification that integrates phlogopite into the current classification of ultramafic rocks, without modifying the already accepted terminology or the classificative criteria (i.e. the mineral modal abundances). Phlogopite is added as an endmember in the ultramafic rocks classification diagrams, changing their shapes from triangular to tetrahedral. The new tetrahedral classification has also been implemented, in relation to the hornblende-bearing ultramnafic rocks, to include both ortho- and clinopyroxene at the vertices of the diagram, combining the Ol-Opx-Cpx and Ol-Px-Hbl diagrams. This allows a more specific and accurate classification of samples. An excel spreadsheet containing the new diagrams and a macro that automatically classifies the rocks is presented.

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### Intrusion of Gabbroic Dykes in the sub-continental Finero mantle massif: an example of melt-rock interactions at mantle conditions

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Keywords: Gabbroic dyke, Sapphirine, Finero.

The Finero Phlogopite-Peridotite (FPP) is a mantle massif recrystallized through several events of melt migrations. These events have enriched the FPP in crustal components (LILE and LREE) and hydrous phases (amphibole and phlogopite) and they have been suggested to be related to a subduction/post orogenic geodynamic setting. One of the latest metasomatic events is represented by the intrusion of sapphirine-bearing gabbroic dyke swarms. Dykes are formed by a Leucocratic Zone at the nucleus and a melanocratic zone characterized by a cumulus zone (the Early Amph Zone) bounded by two distinct reaction zones (the Opx Zone at the contact with the host and the Late Amph Zone at the contact with the Leucocratic Zone). This structure has been interpreted as a two-steps intrusion process, triggering the interaction of migrating melts with the host peridotite and the first cumulates. In the first step, the melt reacts with the FPP rocks forming the Opx Zone and evolves by fractional crystallization of amphibole cumulates. In the second step, an evolved melt reacts with the first cumulates producing metasomatic sapphirine and segregating plagioclase-rich bands containing abundant apatites at the nucleus of the dikes.

New O, Sr and Nd isotopes on minerals suggest a more complex evolution.

The  $\delta^{18}$ O increases from 5.81‰ in orthopyroxenes at the dykes' border to ~6.90‰ in cumulitic amphiboles and 8.60‰ in plagioclases. The <sup>87</sup>Sr/<sup>86</sup>Sr values for plagioclase and coexisting apatite show isotopic disequilibrium between the two phases. Similarly, Nd isotopic values suggest disequilibrium between plagioclase and at least one amphibole generation. These isotopic variations could be explained with a progressive contamination of the parent melt of the gabbroic dykes during its fractionation through an AFC-like process between mantle-derived melt(s) and a crustal-enriched host (the FPP).

The occurrence of abundant apatite and carbonate inclusions, together with the alkaline geochemical affinity suggest possible relationships between the gabbroic dykes and other alkaline/apatite-rich metasomatic events in the Finero Complex. This evidence correlates the gabbroic dykes' intrusions in the FPP with Triassic alkaline dykes within the Finero Mafic Complex, and the general Triassic alkaline magmatic activity recorded in the Ivrea-Verbano Zone.

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# The Geochemistry of the melilite-bearing lavas of the Nyiragongo volcanic complex (D.R. Congo)

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Keywords: Nyiragongo, olivine melilitites, lithosphere.

The extremely active Mount Nyiragongo, located in the Virunga Volcanic Province on the edge of the Tanzanian craton, is formed by highly silica undersaturated, feldspar-free, melilite-bearing rocks (olivine melilities and melilite-leucite nephelinites); nepheline is more abundant than leucite. The Nyiragongo primitive rocks are characterized by high contents of MgO (>8 wt.%), CaO (>12 wt.%) and Sr (>2000 ppm) and low Zr/Nb (2.1). The REE patterns show high La/Yb<sub>n</sub> (42), no negative anomalies in Eu, and the mantle normalized diagrams display troughs at K and Pb. The <sup>87</sup> Sr/<sup>86</sup>Sr (0.70447 - 0.70469), <sup>143</sup>Nd/<sup>144</sup>Nd (0.51272), <sup>206</sup>Pb/<sup>204</sup>Pb (19.413 - 19.751), <sup>207</sup>Pb<sup>204</sup>Pb (15.663 - 15.749) <sup>208</sup>Pb/<sup>204</sup>Pb (39.629 - 39.814) isotope compositions has also been determined. A volatile (H<sub>2</sub>O, CO<sub>2</sub>, S, Cl and F) and incompatible element-rich lithosperic source is proposed also from the evaluation of the isotopic compositions of the lavas, far removed from that of astenosferic or plume mantle, and expected in metasomatized cratonic/pericratonic areas throughout the African plate. Melting was favoured by the rifted tectonic regime and by the decreasing of melting temperature caused by fluid-rich sources. Melilities and nephelinites are silicate melts generated by CO<sub>2</sub>-rich sources, and occur preferentially at the propagation tip and on the flanks of the rifts which impinge on a craton that appears to be at an ntermediate stage of destabilization (e.g., Chakrabarti et al., 2009; Foley et al., 2012; Foley and Fischer, 2017).

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## From crustal protoliths to mantle pyroxenites: a highly siderophile elements and Os isotope perspective from the External Liguride mantle section (N Apennine, Italy)

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Keywords: pyroxenite, siderophile elements, Os isotopes.

Pyroxenites derived from crustal recycling are a major form of mantle heterogeneity. They are believed to play a key role in the magma genesis, contributing to the radiogenic Os signatures within the sources of oceanic basalts. However, natural examples are rare. Here, we present HSE (Os, Ir, Pt, Pd, Re) and <sup>187</sup>Os/<sup>188</sup>Os isotopic systematics of pyroxenites enclosed in fertile mantle sequences of the Jurassic northern Apennine ophiolites. Two case studies are considered: garnet clinopyroxenites and websterites from the Rio Strega-Mt. Prinzera (RS-MP) bodies and spinel pyroxenites from Monte Gavi (MG). We will show that relics of ancient subducted crust are heterogeneous as a consequence of geochemical variability of the protoliths, modification during recycling processes and interaction with the host peridotites, producing centimetre- to metre-scale <sup>187</sup>Os isotopic heterogeneity.

The RS-MP garnet clinopyroxenites have heterogeneous mafic crustal precursors that experienced a longlived evolution of recycling into the mantle (1.5-1.0 Ga) as inferred from Lu-Hf isotope systematics. They originated by crystallization of eclogite-derived melts, whereas the websterites were interpreted as secondary pyroxenites with a crustal geochemical fingerprint and a peridotite wall rock contribution. All the pyroxenites are variably depleted in Os and Ir and enriched in Pt, Pd and Re with respect to the host peridotites. Bulk rock HSE compositions of the garnet clinopyroxenites are consistent with sulphur saturation and sulfide crystallization from partial melts of gabbro-derived eclogites. <sup>187</sup>Os/<sup>188</sup>Os ratios recalculated for the age of a Mesozoic melting event inferred from Nd-Hf isotopes are unradiogenic to slightly radiogenic in the peridotites (0.124-0.134) and moderately to highly radiogenic in the pyroxenites (0.149-2.190). Decoupling between Re/Os ( $T_{Ma} = 2.0-2.8$  Ga) and Lu-Hf isotope systematics may be due to fractionation of Re/Os ratios with no Os isotopic homogenization of the sulfide melt fraction.

At Monte Gavi, a undeformed large body (up to 10 m-thick) of Al-Fe-rich spinel pyroxenites is associated with cm-thick layers of Mg-rich pyroxenites locally containing olivine relics from the host lherzolite. The Fe-rich pyroxenite body has melt-like HSE patterns, whereas the Mg-rich pyroxenites are enriched in Os and Ir. Bulk rock Os isotopes show increasingly radiogenic composition from Mg- to Fe-rich pyroxenites ( $^{187}Os/^{188}Os_{165Ma} = 0.185-0.518$ ). The MG pyroxenites may have formed by crystallization of melts derived from "aged" eclogite-rich sources. The thick pyroxenite body represents a melt-dominated system, whereas the thin pyroxenite layers derived by melt/peridotite hybridization.

In both occurrences, the host peridotites show nearly flat chondrite-normalized HSE patterns, possibly suggesting a history of depletion in incompatible HSE such as Pd and Re followed by refertilization through interaction with the pyroxenite-forming melts.

### Emplacement of the huge Zn-Pb-Ag vein system of Montevecchio, Arburese (SW Sardinia): geological, mineralogical, geothermometric and isotopic inputs towards a new metallogenic model

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Keywords: Pb-Zn-Ag veins, sphalerite microchemistry, microthermometry.

The Montevecchio-Ingurtosu district (SW Sardinia) was one of the largest Pb-Zn producers of Italy between 1878 and 1968, with important yields of Ag and other byproducts (Cd, Ge, In, Ni, Co). Nonetheless, detailed studies of the Montevecchio orebodies and mineral assemblages are surprisingly scarce and old. Mineralization is hosted in a NE-SW-trending, 10 km-long set of steep veins emplaced parallel and radial to the contact of the Variscan Arburese granitoid complex. Host rocks are Paleozoic low-grade metapelites and metavolcanics variably affected by contact metamorphism. Recently the ore system was systematically sampled and analyzed for major to trace elements, microthermometry and stable isotopes (on carbonates). Different ore types were observed, not necessarily belonging to the same ore system. The Montevecchio ore consists of galena and sphalerite with minor Ag-Cd tetrahedrite, chalcopyrite, accessory Co-Ni sulfarsenides, minor pyrite and rare Au in quartz, Fe-Mn-Zn carbonate or barite gangue. Other ore types found contain galena with Cdrich sphalerite plus scheelite, or Fe-rich sphalerite, pyrrhotite, argentite and rutile in calcite-adularia-fluorite gangue. The new studies reveal some intriguing aspects of the Montevecchio assemblages. Major and trace elements redistributed among sulfides and sulfosalts according to complex patterns. Ghost microtextures in quartz gangue and rhythmic Fe and Zn-rich growth zones in primary carbonates suggest multistage deposition. Galena reveals ubiquitous, extreme enrichments in sub-µ mono/polyphase sulfosalt blebs. In zoned sphalerite partitioning of minor and trace elements (Fe, Cd, Mn, Ag, Co, Ni, Cu, Pb, Ge, In, Sn, Se, Pd and Rh) may vary in different veins. Cd, Ag and Ge also partition into tetrahedrite during polyphase deposition, depending on galena abundance. Microthermometry on fluid inclusions in sphalerite and ore-related quartz and based on trace elements in sphalerite (Frenzel et al., 2016) suggest deposition by high-salinity fluids between 160° and and 220°C for the Montevecchio system (in agreement with stable isotope signatures of siderite), while sphalerite in the other ore types records higher temperatures (360°-440°C). Different ore assemblages marked by distinct thermal conditions and ghost textures, coupled with widely variable Pb isotope signatures for Montevecchio ore suggest the existence of an early, minor, probably granite-related "ghost" ore phase overprinted by the huge flood of metal-loaded hypersaline fluids of unknown origin and moving across regional-scale tectonic corridors. The same crustal-scale tectonic pattern that controlled magma ascent and emplacement in the Arbus igneous complex at 304 Ma was probably critical in focusing these late mineralizing fluids.

Frenzel, M., Hirsch, T. & Gutzmer, J. (2016): Gallium, germanium, indium, and other trace and minor elements in sphalerite as a function of deposit type. A meta-analysis. Ore Geol. Rev., 76, 52-78.

## The Ni-Co-As-Ag-Bi-rich hydrothermal vein ores of the Arburese district (SW Sardinia, Italy): mineralogical and geochemical characterization of possible sources for critical metals

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Keywords: Ni-Co arsenides, five-element veins, hydrothermal breccias.

The southern Arburese region (SW Sardinia) hosts a wide variety of ore deposits of historical importance but sofar rather poorly known. The deposits range from Pb-Zn skarns to Fe-As, Sn, Pb-Zn and Ni-Co-As-bearing hydrothermal veins. They are emplaced in an Ordovician/Devonian very low grade metasedimentary sequence (pelites, black shales and limestones) belonging to the Variscan Foreland, along a mineralized corridor close to the contacts with the late-Variscan Arbus and Monte Linas igneous complexes. Among them, a Ni-Co-As-Ag-Bi-rich vein system may be traced for over 6 km in E-W direction, across the Sa Menga, Acqua Is Prunas, Fenugu Sibiri and Pira Inferida abandoned mines. The Ni-Co system crosscuts the As-rich Punta Santa Vittoria vein system. Ore petrography and microchemical analyses were carried out to define assemblages and main geochemical signatures of the different orebodies. The Ni-Co-As veins consist of dominant Ni-Co sulfarsenides and arsenides with varying amounts of Pb-Cu-Zn sulfides and sulfosalts (galena, transparent Cd-rich sphalerite, tetrahedrite, chalcopyrite, bournonite) in quartz-siderite gangue cementing pelitic/black shale breccia. Mineralization is polyphasic and displays textures with centimetric spheroidal nodules composed of niccolite-breithauptite solid solution or sphalerite cores including droplets of native Bi, and overgrown by concentric crusts of sulfarsenides, diarsenides or sulfides. Ag is enriched in tetrahedrite and acanthite, while Au blebs are disseminated in the external sulfarsenide crusts. Major sulfides contain detectable amounts of selenium. The Punta Santa Vittoria As-rich vein system consists of arsenopyrite in highly strained quartz gangue with minor chalcopyrite, Fe- and Cd-rich sphalerite and inclusions of accessory native Bi, pyrrhotite, cubanite, bismuthite, Se-rich galena and Pb-Ag-Bi-Se sulfosalts. As, Se, Bi and Ag contribute to link these two ore systems distinguished by mineralogical features and geothermometry. Textures and temperature estimates based on sphalerite and arsenopyrite-pyrrhotite assemblages suggest rather high crystallization temperatures, up to 450 °C, for the Fe-As vein. A lower range, close to 250 °C, is suggested for Ni-Co-As mineralization, based on cockade textures, fluctuating Co/Ni ratios in the (Ni,Co)As nodules and low-Fe sphalerites, compatible with preliminary microthermometric analyses. C-O stable isotope analyses on siderite gangue confirm this thermality and suggest deposition in relatively reducing conditions. Ni-Co-As ores of SW Sardinia are analogous to the uncommon and strategically interesting Five Elements Veins, Ni-Co-As/ Sb-Ag-Bi, type deposits. Possible sources of metals, especially Ni and Co, are discussed in reference to the Variscan igneous complexes. Moreover, the occurrence of Se-bearing minerals in this part of Sardinia may represent a direct link with late-Variscan Se-rich ores of SE Sardinia (e.g. Baccu Locci mine, Gerrei district).

## Vanadium stable isotopes and trace element concentrations of Reykjanes Ridge basalts: Investigating mantle oxygen fugacity, melting processes and lithological heterogeneities

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Keywords: mantle melting, MORB, oxygen fugacity.

Mid ocean ridge basalts (MORBs) are the most abundant lavas on Earth covering  $\sim 70$  % of the surface. They are produced by adiabatic decompression partial melting of mantle peridotite at spreading centres and by studying their composition the physical and chemical properties of the deep mantle can be inferred. Oxygen fugacity (fO<sub>2</sub>) is a vital property that governs melting processes, mass transport and speciation of volatile species in the mantle and therefore its precise knowledge is key to understanding the formation and evolution of the solid Earth and its atmosphere.

Trace element (e.g. V/Sc) and Fe<sup>3+</sup>/Fe<sub>tot</sub>, ratios of MORBs have been used as mantle fO<sub>2</sub> proxies but provide contrasting results (Lee et al., 2005, Cotrell & Kelley, 2013). New, non-traditional stable isotope systematics of transitions metals such as vanadium, on the other hand, are proposed as possible alternatives to investigate mantle fO<sub>2</sub> (e.g. Prytulak et al., 2013).

In this study we analysed 64 well-characterized MORBs from a 700 km-long transect of the Reykjanes Ridge that display systematic variations of trace elements and and  $Fe^{3+}/Fe_{tot}$  with distance from Iceland (e.g. Murton et al., 2002, Shorttle et al., 2015), providing an ideal case for examining mantle fO<sub>2</sub> proxies. New trace element concentrations were determined on all glasses by precise Laser Ablation Ion Couple Mass Spectrometry (LA-ICPMS) analyses. A suite of 20 samples, covering the entire section of the Reykjanes Ridge and the observed  $Fe^{3+}/Fe_{tot}$  content, was further selected for vanadium stable isotope analyses that were performed by Multi Collector Ion Couple Mass Spectrometry (MC-ICPMS).

We combine the new geochemical data with thermodynamic melting models to identify the effect of lithological heterogeneity, melting and fractional crystallization on the trace element and isotopic composition of Reykjanes Ridge basalts and improve current estimates of mantle  $fO_2$ .

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## Pyroxenites as key component in the veined MORB mantle source: insights from the Ligurian mantle (Italy)

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Keywords: pyroxenite, melt-peridotite reaction, mantle heterogeneity.

Pyroxenites have been largely advocated as enriched isotopic component in the veined mantle source of oceanic basalts. Recent works have emphasized the role of "secondary pyroxenites", i.e. pyroxenites generated by reaction between peridotites and pyroxenite-derived melts. Such Mg-rich secondary pyroxenites are expected to possess major element composition and melting relationships similar to peridotites, with enriched trace element and isotopic signature, possibly inherited by their origin as recycled oceanic crust and/or as "aged" igneous lithospheric veins (e.g. Lambart et al., 2013). Few natural and experimental studies documented the geochemical signature, origin and potential role in mantle melting of such "hybrid" lithologies. Here we discuss the results of on-going investigations in the External Liguride ophiolitic mantle peridotites (Northern Apennine, Italy), ideal proxy of a MORB fertile mantle, containing abundant secondary-pyroxenite layers (Borghini et al., 2013, 2016). Sm-Nd and Lu-Hf isotope studies indicate that pyroxenites constitute old (Ordovician) intrusion events that have induced systematic trace element enrichment in the host mantle, as a consequence of reactive percolation by pyroxenite-derived melts. Over time, this resulted in significant Nd and Hf isotopic changes in the infiltrated peridotites, encompassing the global isotopic variability of MORBs. Moreover, pyroxenites exhibit an overall significant Nd and Hf isotopic variation, covering both enriched and depleted compositions. Such Hf isotopic signatures are mostly consequence of very heterogeneous HREE and Lu/Hf ratios (in both cpx and whole rocks), likely inherited by primary garnet (absent in the present mineralogy). Parallel experiments have indicated high melt productivity of such secondary pyroxenite (Borghini et al., 2017), which produces basaltic melts differing from peridotite-derived melts only for lower Na<sub>2</sub>O and higher CaO contents. Computed melt compositions assuming mixed fertile lherzolite - secondary pyroxenite mantle sources (5-50% pyroxenite mass fraction in the source) match the major element chemical variability defined by primitive MORBs, thus representing a hidden major element component in the mantle source. Our results reinforce the idea that secondary pyroxenites constitute dynamic upward propagation of deeper mafic heterogeneities, capable to amplify the isotopic heterogeneity of a veined mantle source, both by their occurrence as "extreme" (either enriched or depleted) isotopic components, and by the isotopic changes they can induce over time in the host peridotite. Overall, this supports the relevant role of secondary pyroxenite components to explain the isotopic variability of MORBs.

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#### Melt-rock reaction at the oceanic mantle- crust transition: evidence from highly siderophile and chalcogen elements in troctolites from the Jurassic alpine ophiolites

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Keywords: Os isotopes, highly siderophile elements, olivine-rich troctolites.

Reaction of migrating melts with lithospheric mantle and lower crust and fractional crystallization most likely shape the chemistry of erupted ocean ridge basalts. At the mantle-crust transition this process is typically related to formation of olivine-rich troctolites (ORT), whose petrogenesis is generally attributed to reaction between an olivine-rich matrix and a migrating MORB-like melt crystallizing plagioclase and minor clinopyroxene. The original olivine-rich matrix may be formed by previous melt-mantle reaction or by olivine crystallization from primitive precursor magmas.

This study reports whole-rock highly siderophile (HSE: Os, Ir, Ru, Rh, Pt, Pd, Au and Re) and chalcogen (S, Se and Te) element compositions, and Re-Os isotopes of ORT included within lower crust sequences from Jurassic Alpine ophiolites. Selected samples were previously studied by Renna & Tribuzio (2011), Renna et al. (2016), Sanfilippo & Tribuzio (2013). The chalcophile element data were examined to (i) detect crustal vs. mantle contributions and (ii) constrain the effect of melt-rock reaction on the HSE and other chalcophile elements.

The ORT have similar Primitive Mantle (PM)-normalized HSE-Te-Se-S patterns showing a gradual increase of normalized concentrations from Os to Au (similar to Mg-rich magmas such as picrites or komatites), and nearly flat Au-Te-Se-S patterns. These rocks have the highest HSE, S, Se and Te contents among primitive lower crustal rocks, thereby implying that they might be an important repository for some HSE within the lower oceanic crust (e.g., Os, Ir). Initial  $\gamma$ Os (160 Ma) range from +0.2 to +5.9 and overlap with data on MORB glasses and typical Phanerozoic mantle values. The  $\gamma$ Os data extend to slightly suprachondritic values that are uncommon in Jurassic Alpine mantle peridotites. Thus, ORT may have an entirely crustal origin, or melt-rock reaction overprinted and partially removed the original mantle inventory of Os isotopes in these rocks. The PM-like S-Se-Te ratios in some ORT could support the latter interpretation, as they require that the magmas that formed the ORT were originally sulfide-undersaturated and only reached saturation during the formation of ORT. Thus, the crust-mantle transition below ocean ridges acts as a reactive filter that may significantly change the <sup>187</sup>Os/<sup>188</sup>Os, chalcophile and compatible element chemistry of ocean ridge basalts.

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### Noble gases and CO<sub>2</sub> in fluid inclusions from lithospheric mantle xenoliths

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Keywords: Noble gases, CO<sub>2</sub>, Mantle.

The investigation of mantle-derived products coming from Sub Continental Lithospheric Mantle (SCLM) is crucial for constraining its geochemical features and evolution, and for better evaluating the information arising from the study and monitoring of volcanic gases. A significant contribution in the comprehension of the mantle features may come from the study of fluid inclusions (FI) geochemistry in ultramafic xenoliths. Several researches have already demonstrated that noble gases (He, Ne, Ar) and  $CO_2$  systematics in FI represent an useful tool for understanding the main processes that modify in time and space its original features (Deines, 2002; Gautheron et al., 2002, 2005; Martelli et al., 2011, 2014; Correale et al., 2012, 2015; Gennaro et al., 2017). However, the contemporarily measurement of helium, neon, argon, and  $CO_2$  concentrations and isotope ratios in mantle xenoliths is limited to a few suites of samples.

This work proposes an update of knowledge coming from the integrated study of petrography and geochemistry of the minerals with noble gases and  $CO_2$  (when available) in FI from lithospheric mantle xenoliths. We aim to show how processes of partial melting, metasomatism, refertilization, magmatic degassing, volatile recycling, and mixing may modify the pristine composition of fluids stored in SCLM and give clues on the geodynamic evolution. We focus but not limit on the European area that has experienced extensive volcanic activity related to its complex geodynamic evolution.

As a possible outcome, we argue that this approach may help in better comprehend the  $CO_2$  cycle in the mantle.

### Thirty years of the ternary diagram Na-K-Mg (Giggenbach, 1988): applications and limits

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Keywords: geo-thermometer, thermal waters, water-rock interaction.

In the last decades, a growing number of works has increasingly focused on the study of thermal waters using the approach described in the pioneering work of Giggenbach (1988). The ternary diagram Na-K-Mg represents one of the most used tool for the graphical evaluation of deep temperature in geo-thermal systems. In spite of its wide use, the pristine approach proposed by Giggenbach (1988) included several constraints for the successful application of the method. In Giggenbach (1988), thermal-water composition is used to classify groups of water and their origin, and to prove if water-rock equilibrium (i.e the equilibrium conditions, water-rock interaction implies the simultaneous existence of dissolution, precipitation and exchange processes under given temperature, pressure and salinity conditions. If the equilibrium is only partially attained or other processes are involved as well as fluids with different compositions (e.g. seawater, cold brines, connate fluids), the ternary diagram Na-K-Mg might not provide useful information. Details on the method and some application examples will be discussed.

Acknowledgments: P.R is deeply grateful for the support received from INGV and PO\_FSE Sicilia 2014-2020 project.

Giggenbach, F.W. (1981): Geothermal mineral equilibria. Geochim. Cosmochim. Acta, 45, 392-410.

Giggenbach, F.W. (1988): Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. Geochim. Cosmochim. Acta, 52, 2749-2765.

## Are the refractory mantle peridotites from Monte Civrari (W Alps) of subcontinental or abyssal origin?

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Keywords: Alpine ophiolites, mantle geochemistry.

Here we present mineralogical, geochemical and Nd-Pb isotope data for the ophiolitic mantle body of Monte Civrari, which is exposed west of the Lanzo Massif. The outcrops of Monte Civrari are mainly composed of antigorite serpentine schists with decameter-sized lenses of exceptionally fresh mantle peridotites locally intruded by small veins of rodingitized metagabbros. The samples of this study are medium- to coarse-grained spinel harzburgites to cpx-poor lherzolites (Cpx < 5 vol %). They generally show a protogranular texture. The spinels frequently form clusters with orthopyroxene  $\pm$  clinopyroxene, possibly as products of garnet breakdown. The clinopyroxene (Mg# 90-91) show very low TiO<sub>2</sub> (0.05-0.15 wt. %) and Na<sub>2</sub>O (< 0.1 wt. %) coupled with high Cr<sub>2</sub>O<sub>2</sub> contents (1.2-1.5 wt%). Spinels have compositions similar to those of abyssal peridotites, with Cr# and Mg# varying between 0.32-0.34 and 0.68-0.71, respectively, and low TiO<sub>2</sub> contents (0.05-0.10 wt%). Most samples do not show any evidence of interaction with melts and preserve highly refractory chemical compositions. The clinopyroxenes display strongly fractionated REE spectra ( $Ce_N/Yb_N \sim 0.001$ ), with prominent LREE depletions ( $Ce_N/Sm_N = 0.004-0.005$ ) and low HREE abundances ( $Yb_N \sim 5-6$ ) associated with HREE fractionation ( $Gd_N/Yb_N = 0.4-0.5$ ). Clinopyroxene REE compositions may be reproduced by small amounts  $(\sim 5-6\%)$  of fractional melting of a garnet lherzolite precursor followed by 10% melting in the spinel peridotite field. As a whole, Pb isotope compositions of bulk rocks fall in the fields of global MORB and plot close to the 4.53 Ga reference isochron. Nd isotopes of clinopyroxenes confirm the presence of refractory mantle domains with old ages of depletion in the Ligurian Tethys oceanic lithosphere. The origin of these mantle domains has been previously attributed to incorporation of SCLM derived from a late Variscan DMM melting event (see Mc Carthy & Muntener, 2015 and quoted references). However, geothermometry based on trivalent REE+Y exchange between clino- and orthopyroxene, yields high T estimates (TREE) of 1170-1300°C, associated with high T values obtained applying Ca-in Opx (1200-1280°C) and pyroxene solvus methods (TBKN ~ 1100°C). Thermal evolution of the Monte Civrari mantle body is thus consistent with rapid cooling and exhumation from asthenospheric conditions, similar to modern abyssal type peridotites, which apparently argues against a long residence time in the SCLM after the Permian event.

McCarthy, A. & Müntener, O. (2015): Ancient depletion and mantle heterogeneity: Revisiting the Permian-Jurassic paradox of Alpine peridotites. Geology, 43, 255-258.

#### Melting the heterogeneous mantle: messages from replacive mantle bodies

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Keywords: MORB, mantle peridotite, dunite.

The Earth's mantle beneath ocean ridges is commonly thought to be heterogeneous, with portions enriched in incompatible elements and portions of ancient, depleted asthenosphere preserving highly refractory compositions (Stracke et al., 2011). Owing to the scarcity of mantle samples, this compositional heterogeneity has mainly been studied through melts erupted on the surface. However, systematic comparisons between abyssal peridotites and basalts show that the mantle melts are generally mixed prior to their eruption to the surface, erasing some of the compositional heterogeneity of the source material (Salters et al., 2011). The style, depth and physical mechanism of melt migration thereby fundamentally influence the trace element and isotope ratios of the erupted melts. A wide range of observation suggest that melt extraction and magma migration are processes occurring in spatially confined high permeability channels (Kelemen et al., 1995). If erupted melts are not fully representative of the heterogeneity of the mantle source, high permeability migration channels better offer a portrait of the chemical variability of melts extracted from the source region. In this contribution we discuss the chemical heterogeneity of the replacive bodies from an ophiolitic mantle section exposed in the Western Italian Alps (Lanzo South, Massif). Using trace elements and Nd-Hf isotope data we show that melts forming these replacive bodies were extremely heterogeneous compared to aggregated MORB, spanning form enriched to very depleted compositions and thus most likely produced by different mantle domains.

Kelemen, P. B., Shimizu, N. & Salters, V.J.M. (1995): Extraction of mid-ocean-ridge basalt from the upwelling mantle by focused flow of melt in dunite channels. Nature 375, 747-753.

Salters, V.J.M., Mallick, S., Hart, S.R., Langmuir, C.H. & Stracke, A. (2011): Domains of depleted mantle; new evidence from hafnium and neodymium isotopes. Geochem. Geophys. Geosyst. doi:10.1029/2011GC003617.

Stracke, A., Snow, J.E., Hellebrand, E., von der Handt, A., Bourdon, B., Birbaum, K., Gunther, D. (2011): Abyssal peridotite Hf isotopes identify extreme mantle depletion. Earth Planet. Sci. Lett., 308, 359-368.

#### Radon and carbon gas anomalies along the Watukosek Fault System and Lusi mud eruption, Java Island, Indonesia

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Keywords: Lusi mud eruption, Gas migration origin, Preferential leakage pathways.

An extensive survey was carried out in the Sidoarjo district (East Java, Indonesia) to investigate the gas leaking properties along fractured zones coinciding with a strike-slip system, the Watukosek Fault System in NE Java. This structure has been the focus of attention since the beginning of the spectacular Lusi mud eruption on the 29<sup>th</sup> May 2006. This sinistral strike-slip fault originates from the Arjuno-Welirang volcanic complex, intersects the active Lusi eruption site displaying a system of antithetic faults, and extends towards the NE of Java where mud volcanic structures reside.

In the Lusi region we completed a geochemical survey along three profiles combining measurements of a)  $^{220}$ Rn and  $^{222}$ Rn activity, b) CO<sub>2</sub> and CH<sub>4</sub> soil gas content, c) CO<sub>2</sub> and CH<sub>4</sub> fluxes, and d) gas analyses.

The profiles are up to  $\sim 1.2$  km long and intersect perpendicularly areas with intense fracturing and surface deformation along the WFS. The purpose was to investigate the presence and origin of soil degassing activity in potentially active fault zones.

Results show that the peripheral sectors of the profiles have high <sup>220</sup>Rn activity and reduced CO<sub>2</sub> and CH<sub>4</sub> fluxes and concentrations. This suggests low fluids migration that could be affected by shallow circulation. In contrast, the segments of profiles intersecting the fractured zones have the highest <sup>222</sup>Rn activity, CO<sub>2</sub> and CH<sub>4</sub> flux and gas concentration values. The relationship existing among the measured parameters suggests that the WFS acts as a preferential pathway for active rise of deep fluids. The presence of such advective processes is suggested by the relatively high rate of migration needed to obtain anomalies of short-lived <sup>222</sup>Rn in the soil pores. Gas molecular and isotopic composition reveals that all sampled localities have a mixed hydrocarbon origin implying the presence of shallow microbial and deeper thermogenic hydrocarbons. CO<sub>2</sub> isotopic values indicate the presence of mantle derived CO<sub>2</sub> and thermo-metamorphic CO<sub>2</sub> suggesting that elevated temperatures have a key role in this active system. The samples collected from fractured and faulted zones reveal to have gas composition similar to that obtained from Lusi crater, indicating deep origin fluids.

Sciarra, A., Mazzini, A., Inguaggiato, S., Vita, F., Lupi, M. & Hadi, S. (2018): Radon and carbon gas anomalies along the Watukosek Fault System and Lusi mud eruption, Indonesia. Marine and Petroleum Geology, 90, 77-90. <u>https://doi. org/10.1016/j.marpetgeo.2017.09.031</u>.

## Geochemical variations of gas composition and C isotopic signature in the Modena province during and after the 2012 Emilia seismic sequence

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Keywords: Geochemical studies, Leakage pathways, Seismic sequence.

Soil gas anomalies represent an useful tool to highlight the constrains that surface features (soil characteristics, buried geological structures etc) act on natural gas migration. The study of gases with origin and physical/chemical behavior, the collection of a large number of samples during the dry season (under stable meteorological conditions) and the use of proper data analysis are fundamental in the comprehension of gas migration mechanism. Following this approach the spatial distribution of these anomalies may represent an important and suitable tool for identifying active tectonic structures, especially in areas were alluvial deposit prevent the direct observation of sismogenic structures.

Several geochemical surveys (soil gas and shallow water) were carried out in the Modena Province (Massa Finalese, Finale Emilia, Medolla and S. Felice sul Panaro), during the 2006-2015 period. In May-June 2012, a seismic sequence occurred closely to the investigated area. In this area, 150 soil gas concentrations and 30 shallow waters (dissolved gasses) were sampled in April-May 2006, May-July 2008, and repeated in May and September 2012, June 2013, July 2014 and June 2015.

Beside soil gas composition, measurements were also carried out on methane and carbon dioxide isotopes. We found that soil gas concentrations markedly changed during the main shocks of May 20 and 29, 2012 (Mw 6.1 and 6.0, respectively), highlighting the presence of a buried fault intersecting the gas vents. We suggest that crustal dilation associated with seismic activity favored the uprising of geogas towards the surface.

Changes in the isotopic signature highlight the contribution of two distinct sources, one deeper, thermogenic and another superficial related to organic-rich layer, whose relative contribution varied before, during and after the earthquake. This is likely due to an increase of microbial component due to the ground shaking of the shallower layers during the seismic sequence, covering the thermogenic contribution. Geochemical surveys highlight the importance to carry out a discrete monitoring that can help to study the stress/strain changes related to seismic activity that may force crustal fluid to migrate up, thereby altering the geochemical characteristics of the fault zone at surface before and after earthquakes.

Although the changes we detected are specific for an alluvial plain, we suggests that analogous processes may be active elsewhere, and that soil gas geochemistry represents an useful tool to discriminate the gas migration related to seismic activity.

Sciarra, A., Cantucci B. & Coltorti M. (2017): Learning from soil gas change and isotopic signatures during 2012. Emilia seismic sequence. Scientific Reports, 7(1), 14187. DOI:10.1038/s41598-017-14500-y.

#### Archean amphibole as a proxy for the ancient Earth's volatile budget

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Keywords: Archean mantle, Amphibole, Volatile elements.

The poor knowledge on the Archean mantle composition arises a series of problems spanning from the effective chondritic composition of the Earth to how volatile elements (hydrogen, oxygen, chlorine and fluorine) were added to the Earth and how their deep cycle evolved giving origin to life. Because the Archean mantle is scarcely preserved, Archean komatiites and few other mantle-derived rocks are nowadays the only source of information on the Archean mantle composition. However, these rocks generally have strong metamorphic overprints that cause the bulk rock composition to be weakly representative of the original chemical signature, in particular for volatiles and elements with high fluid mobility. A novel approach in this study consists in deriving the volatile components of the mantle from hydrous accessory minerals of Archean ultramafic rocks. Primary amphibole is occasionally an accessory phase of Archean komatiite rocks and, for its capability to incorporate almost all the petrologically relevant elements (e.g., V, Nb, Ta and LILE) and volatiles, it is an important source of information on the geochemistry of the Archean mantle.

We selected amphiboles from ultramafic rocks in the Agnew-Wiluna (Australia, 2.7 Ga) and Abitibi (Canada, 2.7 Ga) greenstone belts and in the Pechenga Complex (Russia, 1.98 Ga). Phanerozoic analogues were also investigated for comparison and to monitor secular changes in mantle volatile signature. All amphiboles were characterized for major and trace element composition by EMPA and LA-ICP-MS. The volatile contents (H<sub>2</sub>O, F, Cl),  $\delta D$  and  $\delta^{18}O$  isotopic signatures were determined by ion microprobe. H<sub>2</sub>O contents reveal that Archean and Phanerozoic amphiboles have a significant dehydrogenation ( $^{O3}O^{2-}$ ) and crystallized from melts with similar water contents. The  $\delta D$  of Archean amphiboles is close to mantle values suggesting that water has a deep origin. However,  $\delta^{18}O$  values of the Archean amphiboles are generally significantly lower than those of Phanerozoic amphiboles in equilibrium with mantle melts. The light  $\delta^{18}O$  in Archean amphiboles could be related to contributions of sea-water and/or high temperature hydrothermally altered oceanic crust. This process is however unlikely given the mantle signature of the  $\delta D$ . The low  $\delta^{18}O$  values could be instead a further evidence of the presence of inhomogenized residues from an early Earth magma ocean in the Archean mantle as proposed to explain the light oxygen isotope signature of olivine in the Weltevreden komatiites (Byerly et al., 2017).

Byerly, B.L., Kareem, K., Huiming Bao, H. & Byerly, G.R. (2017): Early Earth mantle heterogeneity revealed by light oxygen isotopes of Archaean komatiites. Nat. Geosci., 10, 871-875.

## High-pressure relics within a mantle body enclosed in the middle continental crust of the Ivrea crustal section

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Keywords: mantle, pyroxenite, eclogite.

The South Alpine domain of northwest Italy exposes a nearly complete section of the continental crust. The present study deals with a lens consisting of mantle peridotites and amphibolites (1.5 km long and up to 400 m thick) enclosed at mid crustal levels (Alpe Morello locality), along the tectonic boundary separating the Ivrea-Verbano Zone from the Strona-Ceneri Zone. The Alpe Morello mantle peridotites show a widespread recrystallization under tremolite-chlorite facies metamorphic conditions, with a main foliation that is concordant with the hornblende + plagioclase foliation of adjacent amphibolites. The peridotite-amphibolite association is enclosed within sillimanite-bearing, amphibolite facies metasediments. The amphibolite facies metamorphism most likely developed in response to the post-collisional Variscan evolution, before a major event of magmatic underplating dated at ca. 290 Ma. The entire Alpe Morello rock sequence is locally crosscut by peraluminous granitoid dykes that are genetically related to nearby plutons dated at ca. 280 Ma.

The mantle peridotites frequently includes pyroxenite and gabbro layers that locally retain relics of mineral assemblages predating the amphibolite facies regional metamorphism. Primary textures and mineral chemical compositions document that the layers formed by intrusion of MORB-type melts giving rise to clinopyroxenite to gabbronorite protoliths. Transition of these rocks to eclogite facies conditions is shown by formation of Mg-rich garnet in Al-rich pyroxenites, and of Mg-rich garnet + Na-Ca-clinopyroxene (+ accessory rutile and kyanite) in gabbronorites. The eclogite facies metamorphism was followed by development of granulite facies assemblages, characterized by accessory spinel and sapphyrine in the pyroxenites and the gabbronorites, respectively. The amphibolites adjacent to the mantle peridotites show: (i) evidence for being formed by gabbronorite layers within the mantle peridotites. Isotopic analyses are currently in progress to establish if the pyroxenites, the gabbros and the amphibolite protoliths developed from primitive melts with similar compositions, and to obtain age information about intrusion and eclogite to granulite facies relics in the middle continental crust will be examined.

### New classification of carbonatites and inference for a new differentiation process and REE-ore deposits

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Keywords: carbonatite, classification, REE, fluor-ore.

Today old nomenclature is still in use to classify carbonatites, in this study it's proposed a new carbonatites classification. The RHAT language (Petrov & Moskin, 2015) allows chemically classification of the carbonatites through the Rank formulas. Discrete group of samples with similar chemical compositions are then established.

The study focuses on fluorine role, which is a volatile abundant in the parental magma of all carbonatites. However, carbonatite rocks rarely retain notable amount of fluorine. The term fluorcarbonatite is used, but it's not included in the official classification, according to this study, a representative number of carbonatites and silico carbonatites don't show values of fluorine high enough to discretize a fluorcarbonatite, it's more appropriate to define the rocks fluor-calciocarbonatites, etc.

Special concourse of chemical reactions must occur to fix the fluorine in mineral phases, otherwise the fluorine disperses in the atmosphere. The fluorine enters several mineral phases characteristic of carbonatites such as bastnaesite, britholite, pyrochlore, fluorite, fluorapatite and fluorellestadite, which form in different stages of carbonatites development.

All carbonatite types show great enrichment in Ba, Sr, REE, Y, Nb and U and negative anomalies of Eu, Zr, Ti, Th, Rb, Cs, Pb and K. REE- and flour-ore deposits are often associated with carbonatites. The  $\Sigma$ REE content and the shape of REE pattern is a function of carbonatite magma evolution. In diagrams La/Yb vs  $\Sigma$ REE, La/Y vs Nd there are clearly different trends, which show the possible evolution that the parental magma can have with different grades of differentiation (Buhn, 2002). LILE (Rb, Ba, Pb) and large HFSE (Th, U, Ce) elements with high partition coefficients are typically concentrated in carbonatitic liquid during very low partial-melting (Stoppa, 2013).

Ba/Th, Th/Nb, Th/La, Nb/Ce, Ba/Nb, Ba/Sm, and Nb/U ratios are thought to reflect partial melting of a specific mantle composition. In term of mantle end-members carbonatites show isotopic values of Nd, Sr and Pb like those of enriched mantle (EM1, EM2, ITEM). It seems that the source of these carbonatites is in the asthenospheric mantle, possibly related to the plume activity (Bell et al., 2013).

Bühn, B., Rankin, A.H., Schneider, J. & Dulskic, P. (2002): The nature of orthomagmatic, carbonatitic fluids precipitating REE,Sr-rich fluorite: fluid-inclusion evidence from the Okorusu fluorite deposit, Namibia. Chem. Geol. 186, 75-98.

Petrov, T.G. & Moshkin, S. V. (2015): Method RHAT and its implementation in the software package Petros-3. Mod. Inf. Tech.2, 70-80.

Bell, K., Lavecchia, G. & Rosatelli, G. (2013): Cenozoic Italian magmatism-Isotope constraints for possible plumerelated activity. J. South Am. Earth Sci.41, 22-40.

Stoppa, F. & Schiazza, M. (2013): An overview of monogenetic carbonatitic magmatism from Uganda, Italy, China and Spain: Volcanological and geochemical features. J. South Am. Earth Sci.41, 140-159.

#### Oxidation state of Fe in highly refractory mantle peridotites

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Keywords: cratonic mantle, diamonds, oxybarometry.

Refractory peridotites from cratonic settings are considered to have formed by high-degree of melting in the Archean. Despite recent advances in petrologic modelling, phase relations, redox state and geochemical processes in these mantle domains are still poorly understood. This is mainly due to the paucity of mantle xenoliths representing the pristine (not metasomatised) highly refractory mantle and the difficulties in performing high pressure (P) and high temperature (T) experiments in such compositions. In this project, we investigate a suite of natural samples and perform high-P and high-T experiments on synthetic mineral assemblages to better constrain the redox processes in these mantle domains. The natural samples are spinel-bearing harzburgite and dunite mantle xenoliths and primary inclusions in diamonds from the Murowa kimberlite (Zimbabwe), which are rare examples of pristine, highly refractory mantle fragments (Smith et al., 2009). <sup>57</sup>Fe Mössbauer analyses of natural Cr-spinel, garnet, clino- and orthopyroxene, have been performed using the synchrotron Mössbauer source (SMS) available at the Nuclear Resonance beamline ID18, ESRF, Grenoble. The high-P and high-T experiments were performed using a multi-anvil apparatus and starting material resembling the composition of a spinel-bearing harzburgitic xenolith from the Murowa kimberlite. The P-T conditions of experiments cover the range 3-6 GPa and 1000-1400 °C and run products consist of olivine + orthopyroxene + spinel ± garnet. The attainment of equilibrium in these runs is confirmed by the texture and composition of the run products.

One of the main result of this work is the difference in Fe<sup>3+</sup>/ $\Sigma$ Fe in Cr-spinels between mantle xenoliths (0.04-0.09) and diamonds (0.09-0.14). Application of currently available oxybarometers (e.g., Ballhaus et al., 1991) indicates oxygen fugacity (fO<sub>2</sub>) values of 3 log units below the quartz-fayalite-magnetite oxygen buffer (QFM) for the xenoliths and 1 log unit below QFM for the diamond inclusions. Noting that the mantle xenoliths most likely equilibrated in the pressure range 2-3 GPa and inclusions in diamonds imply P > 4 GPa (considering normal cratonic geotherms), this would suggest an increase in fO<sub>2</sub> with depth and anomalously high fO<sub>2</sub>during diamond formation. Notably, the first experimental results show an increase of Fe<sup>3+</sup>in spinel with P at constant T, suggesting that the higher oxidizing conditions estimated for the spinel inclusions in diamonds might be related to a possible overestimation of fO<sub>2</sub>at higher pressures.

Smith, C.B., Pearson, D.G., Bulanova, G.P., Beard A.D., Carlson R.W., Wittig N., Sims K., Chimuka, L. & Muchemwa, E. (2009): Extremely depleted lithospheric mantle and diamonds beneath the southern Zimbabwe Craton. Lithos, 112, 11406-S2032.

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## Session S20 Magma genesis and transport

Conveners AND CHAIRPERSONS Pier Paolo Giacomoni (Università di Ferrara) Gabriele Lanzafame (Elettra, Trieste) Cristina Perinelli (Sapienza, Università di Roma)

#### Mechanisms of lamellar intergrowth in alkali feldspar

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Keywords: sanidine, lamellar intergrowth, cooling rate.

Sanidine is a widespread liquidus phase in K-rich volcanic rocks forming a continuous solid-solution between  $KAlSi_3O_8$  (Ksp) and  $NaAlSi_3O_8$  (Ab) with minor admixtures of  $CaAl_2Si_2O_8$  (An) and  $BaAl_2Si_2O_8$  (Cn) at temperatures above about 600°C. Towards lower temperatures a solvus opens, leading to lamellar unmixing of alkali-feldspar with intermediary composition during cooling.

In volcanic environments fast cooling produces sub- $\mu$ m wide lamellae (cryptoperthite), whereas the comparatively slow cooling in plutonic and metamorphic environments produces several  $\mu$ m to tens of  $\mu$ m wide lamellae (perthite).

However, occasionally alkali feldspars with  $\mu$ m wide lamellae are also observed in volcanic environments. For example, the alkali basalts of the Late Miocene-Pleistocene south-Slovakian volcanic field contain feldspar megacrystals, with compositions scattering along the 700° ternary feldspar solvus over a range of Ab<sub>70</sub>An<sub>25</sub>Ksp<sub>5</sub> to Ab<sub>47</sub>An<sub>3</sub>Ksp<sub>50</sub>. Some of the feldspars show several  $\mu$ m to tens of  $\mu$ m wide K-rich lamellae (Ab<sub>67</sub>An<sub>8</sub>Or<sub>21</sub>Cn<sub>4</sub>) in a Na-rich matrix (Ab<sub>76</sub>An<sub>14</sub>Or<sub>9</sub>Cn<sub>1</sub>). These lamellae cannot be interpreted in terms of exsolution in a closed system. They rather were produced by interaction of a pre-existing Na-rich alkali feldspar with a K-rich melt. This induced in-diffusion of potassium, which drove the feldspar composition into the two-phase field and lead to the nucleation and growth of K-rich feldspar lamellae.

Laboratory experiments have been performed to simulate both processes that may potentially produce lamellar feldspar intergrowth. It was found that closed system exsolution occurs by a spinodal process. At 550°C the wavelength of compositional oscillations is about 17, 20, and 30 nanometres after 4, 8, and 16 days, respectively. Initially, the K- and Na-concentrations vary in a sinusoidal fashion with the composition extremes at  $X_{\rm K} = 0.24$  and 0.59, respectively. Only after 16 days, plateaus developed at these compositions. In contrast, interaction of the same alkali feldspar with a K-rich NaCl-KCl melt at 550°C produced lamellae of K-rich feldspar, while the composition of the feldspar matrix remained largely unchanged. From the beginning, the lamellae had a characteristic spacing of about 5  $\mu$ m, which does not change with time. Initially the K-rich lamellae are only a few hundreds of nanometres wide, and they grow in thickness due to the successive supply of K.

After sufficiently long time, both processes lead to a lamellar intergrowth of K-rich and Na-rich feldspar with quite similar appearance. The underlying processes and the inferences that can be made from the phenomenon are, however, fundamentally different. If spinodal decomposition can be identified by petrographic means, the cooling rate may quantified. If, instead, open system precipitation can be identified, interaction with a K-rich melt can be inferred.

### Carbonatites of Roman Region, genetic relationship with Italian alkaline Rocks

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Keywords: Carbonatites, RHA method, alkaline rocks.

Carbonatites associated with kamafugites rocks type characterize the central Italy magmatism. These rocks occur in several volcanic center localized about 50 Km east of the volcanic complex of the Roman Region (RR) in the Intra-mountain Ultra-Alkaline Province (IUP). Most of IUP occurrences are monogenic, extrusive and of small volume 10<sup>6</sup> to 100<sup>6</sup> m<sup>3</sup> (Lavecchia et al., 2006). The origin of carbonate is essential to define a unique petrogenetic model for Italian rocks. In fact, if is correct the Daly (1910) theory of limestone assimilation (syntexis) and further variants, then it is possible to hypothesize a subduction related model (e.g. Gvirtzman & Nur, 1999). If the carbonate have a primary origin, then it is correct hypothesize a plume model and thinning of the lithosphere (e.g. Bell et al., 2013). We have found two new outcrops of subvolcanic carbonatites at Forcinella (Vulsini district) and at Ficoreto (Sabatini District). The carbonatitic rocks are associated to leucititic rocks and to foid syenites (ejecta). Forcinella and Ficoreto outcrops have similar geological, mineralogical and geochemical characteristics to IUP carbonatites. In particular, they are monogenic vent, with tuffisitic texture (intrusive lapilli tuff). To provide a geochemical representative model of this complex rock association we used Rank Analyses (RHA), this is an information language (Petrov, 2001). The software used to calculate main statistical discriminating factors that resulted as F-C-Ca, Si-Al-Alk, Mg-Fe-P in terms of their atomic% of elements. These factors draft a ternary diagram were the bisector clearly separates analytic data of carbonate and silicate rocks are. The diagram also defines a possible petrogenetic model. Our hypothesis is that silicate rocks and carbonate becomes immiscible starting from a mantle primitive melt. They can erupt along a diatremic path as a mechanical mixture of two magmatic rocks or as physically separate convoys of the two components. If the liquid has a silicate composition it evolves by orthomagmatic differentiation to foid syenites. On the other hands CO,-F-rich fluids have a complex crystallisation history which may range from near magmatic temperature to hydrothermal condition.

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Daly R.A. 1910. Origin of alkaline rocks. Bull. Geol. Soc. Am. 21, 87-118.

Gvirtzman, Z. & Nur, A. (1999): The formation of Mount Etna as the consequence of slab rollback. Nature, 401, 782-785. Lavecchia, G., Stoppa, F. & Creati, N. (2006): Carbonatites and kamafugites in Italy: mantle-derived rocks that challenge subduction. Annals of Geophysics, Supplement to vol. 49, N. 1, 389-402.

Petrov, T.G. (2001): Informative language for description of poly-component object's composition. Scientific-Technical information, 3, 8-1.

## Lithium isotope composition as tracer of crust/mantle interaction at subduction zones: a pilot study to understand the magma genesis of the Plio-Quaternary volcanic areas of Central Italy

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Keywords: Lithium isotopes, Central Italy, Colli Albani Volcanic District.

In the framework of the FISR 2015-2016 "Centro di studio e monitoraggio dei rischi naturali dell'Italia Centrale" project, we carried out a pilot study on the application of the lithium-isotope systematics to selected igneous rocks, in order to shed new light on the nature of subduction components involved in the genesis of magmas feeding the Roman Magmatic Province (Central Italy).

On the Earth, the two lithium isotopes, <sup>6</sup>Li and <sup>7</sup>Li, are susceptible to separation due to their relatively large difference in mass (i.e., fractionation) as natural processes occur. These include mineral formation (chemical precipitation), ion exchange (Li substitutes for Mg and Fe in octahedral sites in clay minerals, with <sup>6</sup>Li preferentially substituted over <sup>7</sup>Li), and rock alteration. Among the available techniques, Thermal Ionization Mass Spectrometry (TIMS) is inherently the most precise method for determination of the Li isotope composition. In the last two decades, considerable progress has been made to minimize mass fractionation during TIMS analysis. To date, no Li investigations have been performed on groundwater and volcanic products from the Italian volcanoes to study water-rock interaction and/or magmatic processes, except for Stromboli volcanics. This study acts as a driving factor towards the utilization of the Li-isotope systematics for future studies, and can be considered as a first step towards the realization of a geochemical database including Li isotopes, integrated with the available Sr, Nd, Pb, Hf, B and O isotopes on Italian Plio-Quaternary volcanic rocks.

The final aim of this pilot study is to test the application of the Li-isotope systematics to shed new light on the geochemical features of the subduction components involved in the genesis of magmas that fed the activity of Colli Albani Volcanic District (Central Italy; e.g., Gaeta et al., 2016 and references therein). This goal will be achieved by analyzing the Li isotope ratios of well-characterized (chemically and isotopically) samples representative of eruptive products of the district, emplaced in the time window from 600ka to 40ka. The activities carried out include: 1. Set up of the procedures to be adopted in clean chemistry laboratory for extracting Li from natural samples; 2. chromatographic separation of Li in the NIST L-SVEC and USGS BHVO-2 (batch #0759) standard samples, after acid dissolution; 3. Set up of the procedures for measuring Li isotope ratios by TIMS.

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Gaeta, M., Freda, C., Marra, F., Arienzo, I., Gozzi, F., Jicha, B. & Di Rocco, T. (2016): Paleozoic metasomatism at the origin of Mediterranean ultrapotassic magmas: Constraints from time-dependent geochemistry of Colli Albani volcanic products (Central Italy). Lithos 244, 151-164.

#### Kinetic crystallization of clinopyroxenes from alkaline basalts: growth rate experiments at high pressure

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Keywords: clinopyroxene crystal growth, alkaline basalt melt, Campi Flegrei.

The kinetics of crystal nucleation and growth are fundamental for the interpretation of rock textures in terms of thermal history of a magma during its ascent to the surface, and to constrain timescales of magmatic processes. In basaltic systems Cpx is a common phenocryst, and due to its wide crystallization range, it contains the most complete record of evolutionary history of a magma. Nevertheless, to date, experimental studies addressed to obtain quantitative measurements of Cpx crystallization kinetics (e.g. crystal growth rate) are few and limited to low pressure conditions ( $\leq$  500 MPa). In this experimental work, we investigated the effects of temperature, water content and dwell time on clinopyroxene (Cpx) crystal growth from an alkaline basalt of the Campi Flegrei Volcanic District (CFVD; Italy) at high pressure. With the aim to provide data on Cpx crystallization kinetics at high pressure, we experimentally investigate a primitive alkaline basalt (APR16 sample, mg# = 0.66 and  $Na_0O+K_0O = 4.4$  wt.%) from Procida island (Italy), representative of the leastevolved rocks of the whole CFVD volcanic products at both anhydrous and hydrous conditions. Experiments were performed at isobaric pressure (800 MPa) as function of temperature (T), water content and dwell time by using the 1/2 inch piston cylinder apparatus at the HP-HT Laboratory of the Earth Sciences Department, Sapienza, University of Rome. We performed a total of 24 experiments divided into three series. Experiments of series 1 were carried out at anhydrous conditions at temperatures of 1250 °C and 1200 °C and dwell time of 0.25, 3, 6 and 9 hours. Experiments of series 2 and 3, instead, were carried out at hydrous conditions (2 and 4 wt.% H<sub>2</sub>O added to the starting material, respectively), temperatures of 1220 °C and 1170 °C (series 2) and 1100 °C and 1050 °C (series 3), and the same dwell time of series 1. Preliminary results show a strong growth rate dependence of temperature and dwell time in both the anhydrous and hydrous experiments. As expected, the charges run at low temperature of each series are more crystallized than those run at high T; moreover, the low-T clinopyroxene grains are generally smaller in size than those formed at high-T. This behavior is noticeable already in the shortest dwell time (0.25 hours) experiments. As regards time, instead, we noted an increase of crystal size with increasing the dwell time (from 0.25 to 9 hours) and a decrease of the number of crystals: this is particularly evident in the hydrous runs (series 2 and 3). Finally, it was possible to note a variation in crystals shape that changes from anhedral/subhedral in the shorter runs to euhedral in the longer ones.

## Viscosity of alkaline basalts at high pressure: constraints on the pre-eruptive system of Campi Flegrei (Italy)

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Keywords: viscosity, melt structure, Paris-Edinburgh press.

The Campi Flegrei Volcanic District (CFVD) includes the Campi Flegrei caldera, the islands of Procida and Ischia, and it is among the most dangerous volcanic systems of the world. The volcanic activity that has characterized the recent eruptive history of the CFVD includes both effusive and hydromagmatic eruptions that resulted in a variety of igneous products from alkaline basalts to trachytes. Among CFVD products, basaltic lava fragments dispersed in the hydromagmatic tuff of the Solchiaro eruption (Procida island) result to be representative of near-primary melts on the basis of their geochemical and isotopical signatures. The knowledge of the viscosity of primitive magmas at high pressure and temperature is needed to model their mobility and ascent rate. These variables allow us to predict the potential volcanic activity at surface. In this study, we investigated the viscosity and melt structure of APR16 alkaline basalt, a lava fragment of the Solchiaro eruption. The anhydrous glassy starting material was prepared at Bayerisches Geoinstitut by using a gas-mixing furnace, by melting the APR16 rock powder at 1400 °C for 15 minutes at atmospheric pressure and oxygen fugacity buffered at Nickel-Nickel Oxide level using a CO/CO<sub>2</sub> gas mixture. Experiments were performed at pressure between 0.7 and 2.3 GPa and temperatures of 1200 °C-1700 °C using the Paris-Edinburgh press combined with synchrotron X-ray technique at beamline 16-BM-B (HPCAT) of the Advanced Photon Source (Argonne National Laboratory, Illinois, USA). Viscosity measurements were conducted with the falling sphere technique. The falling velocity of the platinum probing sphere was measured at each run by ultrafast X-ray radiography using a high-speed camera at 500 frames per second as recording rate. The viscosity was, then, calculated from the Stokes' equation including the correction factors for the effect of the wall and the end effect (Kono et al., 2014). Structural measurements of the liquid at 1700 °C and 2.3 GPa were also performed using multi-angle (20 angle between 3° to 35°) energy dispersive X-ray diffraction technique. Preliminary results show the viscosity increasing from 0.1 to 1 Pa·s as pressure decreases from which an increase in the polymerization during decompression can be inferred. Our results are used to constrain the mobility and ascent velocity of primitive alkaline basalts considered to be parental magmas at Campi Flegrei with important implications for the potential volcanic hazard of the area.

Kono, Y., Park, C., Kenney-Benson, C., Shen, G. & Wang, Y. (2014): Toward comprehensive studies of liquids at high pressures and high temperatures: Combined structure, elastic wave velocity, and viscosity measurements in the Paris-Edinburgh cell. Phys. Earth Planet. Inter., 228, 269-280.

#### Deep magma storage at Mt. Etna. A contribution from petrologic and stratigraphic data of the 1763 flank eruptions

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Keywords: Etna, deep magma, 1763 eruptions.

Mt Etna, the most active volcano in Europe, produces both summit and flank eruptions. During summit and most of the flank eruptions, highly porphyritic lavas are erupted (Porphyricity Index >20% vol) made of plagioclase-rich K-trachybasalts or hawaiites. These petrochemical features are acquired by a magma stored within the central conduit in a shallow region of the volcano's plumbing system (<5 km b.s.l). However a few flank eruptions are different from the above ones, showing a higher explosivity and emitting sub-aphyric (P.I. <20% vol), plagioclase-poor, volatile-rich basaltic magma ascending rapidly from a deeper region (10-12 km b.s.l. or more). These eruptions, which were firstly called "eccentric", were recently renamed as "deep dyke-fed' (DDF) flank eruptions. This terminology better underline their main feature, i.e. they are supplied by dyke-like deep magma intrusions which by-pass the central conduit system of the volcano. Sub-aphyric basalts have been erupted over last 15 ka and during the 1763 (La Montagnola cone), 1974, 2001 and 2002-03 flank eruptions. Since DDF magmas were slightly modified by mixing and fractional crystallization, their study is crucial for identifying the composition of parent magmas, their temporal evolution and the characteristic of the mantle source regions.

In order to investigate further these argumentss we envisaged the 1763 activity which actually consists of two separate eruptions producing: i) ordinary, high porphyritic lavas and Monte Nuovo scoria cone in February on the West flank, and ii) DDF lavas and La Montagnola cone in July-September on the South flank. Indeed, we realized that upwards Mt Nuovo there is another scoria cone named Mt Mezza Luna, associated to a small lava flow whose petrochemistry is consistent with that of a DDF eruption. Field observations and archeomagnetic results show that Mt Mezza Luna and Mt Nuovo formed during distinct, although close in time eruptions. But Mt Mezza Luna alone emitted sub-aphyric basalts whose composition has been compared with that of products from La Montagnola and other DDF eruptions of the last 15 ka (Mongibello volcano). Our data evidence that the DDF magma of the years 1700 is significantly depleted in K with respect to the present one, and that the long-term compositional change of the DDF magma is mainly produced by mixing between different types of deep-seated magmas. Furthermore, the geometry and complexity of the volcano plumbing system in the XVIII century results significantly different from the present one.

### Shallow magmatic and hydrothermal crystallization processes at Piton de la Fournaise (Réunion Island, Indian Ocean) inferred from subvolcanic cognate clasts, xenoliths and xenocrysts

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Keywords: cognate subvolcanic clasts, quartz xenocrysts, Piton de la Fournaise.

La Réunion island is a huge volcanic oceanic system in the southernmost part of the Mascarene Basin (Indian Ocean), 800 km east of Madagascar, which originated from the Deccan Trapps hot spot activity. The island is composed of two juxtaposed volcanic massifs, Piton des Neiges and Piton de la Fournaise (PdF), but a third buried volcano, named Les Alizés, has been recognized below the active PdF and on the eastern submarine flank. Magmas of PdF have an intermediate character between alkaline and tholeiitic, mostly erupted by basaltic effusions (despite some trachyte deposits are present) from its central cone and along the north-east and south-east rift zones. Nevertheless, some violent phreatomagmatic explosive activity generated by magma-water/hydrothermal system interaction may generally occur. The construction of PdF *sensu stricto*, in the south-eastern part of the island, started at about 400/450 ka ago (Lénat et al., 2012).

This study mainly concerns the textural and petrologic study of subvolcanic clasts within the "Bellecombe Ash Member", a large explosive event occurred at ca. 4.5 ky and leading to the formation of the "Enclos Fouqué" caldera. A preliminary thin section study of more than one hundred representative samples emphasizes the presence of many subvolcanic mafic and ultramafic cumulate lithotypes: gabbros, clinopyrossenites and dunites in decreasing order of abundance with various degree of magmatic layering (both in grainsize and modal mineralogy). These cumulates should represent cognates of the erupted magmas, as also inferred from the abundant quenched basaltic glass entrapped interstitially, with no disequilibrium textures induced into the subvolcanic crystal frameworks. Composition of this quenched glass will be investigated through EMP and LA-ICP-MS analyses, in order to infer magmatic processes which have been occurring, shortly before the eruption, during storage and crystallization of the basaltic magma at shallow depth. In addition, microdiorite and dolerite (i.e., microgabbro) samples are also present, the latter showing a large variety of intergranular and ophitic-subophitic microstructures as the result of subvolcanic crystallization processes leading to slowly cooled equivalents of the basaltic magmas i.e. liquidus rather than cumulate composition.

Finally, several quartz xenocrysts, inferred to be crystallized within the PdF hydrothermal system and sampled from other pyroclastic breccias (e.g. Langevin breccia), will be investigated, with special emphasis to fluid inclusions (barometry,  $CO_2$ ,  $H_2O$ , and noble gases), cathodoluminescence and LA-ICP-MS analyses, to unravel the role played by the hydrothermal system during some phreatomagmatic eruptions.

Lénat, J.F., Bachèlery, P. & Merle, O. (2012): Anatomy of Piton de la Fournaise volcano (La Réunion, Indian Ocean). Bull. Volcanol., 74(9), 1945-1961.

## Rapid carbonate assimilation as eruption trigger: new insights from a Somma-Vesuvius (Italy) plinian eruption

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Keywords: carbonate assimilation, Somma-Vesuvius, plinian eruption.

The majority of Italian volcanoes (e.g. Colli Albani, Etna, Phlegrean Fields, Somma-Vesuvius) are settled in carbonate bedrock. Several geochemical (e.g. isotopic composition of gas and volcanic products) and petrological (e.g. presence of skarn and metasomatic rocks, carbonatic fragments within cored bombs) evidence of interaction between magma and limestone has been reported for these volcanic systems. Recently, carbonate assimilation has been object of numerous analytical and experimental investigations focused on currently active volcanoes (e.g. Colli Albani, Merapi, Popocatepetl, Somma-Vesuvius). These studies suggested that this reaction can be very rapid (minutes to days) and can promote the release of large amounts of crustal  $CO_2$ with potential significant consequences for the eruption intensity and eruptive style. Therefore it is critical to estimate the timescale by which this process can occur.

In this study we have explored the role of limestone contamination and its timescale during the Pomici di Base eruption, the oldest and largest explosive event of Somma-Vesuvius. During this eruption (22 ka) a volcanic deposit with a volume  $\geq$ 4.4 km<sup>3</sup> deposit was emplaced from an eruptive column remained stable during the whole plinian phase (column height=16-17 km; MDR=2-2.5x107 kg/s) despite a marked compositional variation from trachytic (~25% of volume) to latitic-shoshonitic (~75% of volume).

Here we have combined 3D textural and geochemical (major-volatile elements and Sr-Nd isotopic ratios) investigations with computational modeling for magmatic contamination able to predict the timescale of isenthalpic assimilation by determining the dissolution rate of limestone. Our results show that the hot (1000-1050°C) mafic (latitic-shoshonitic) portion of magma experienced fast limestone assimilation with a dissolution rate as high as ~1E-4 cm/s through its ascent towards the surface. The resultant rapid CO<sub>2</sub> liberation promoted vesiculation pulses that amplified the eruption intensity despite the magma's low viscosity (~2 Pa s).

We conclude that late carbonate assimilation can strongly affect eruption explosivity on a short timescale with potential implications for geochemical monitoring signals.

#### Ludovico Sicardi, an unknown pioneer of the Volcanic Geochemical Monitoring

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Keywords: Vulcano island, Carapezza, fumarolic field.

On December of 1977, almost 100 years since its last eruption, intense volcanic activity took place in Vulcano Island (Sicily). The elevated fluxes and the temperature increase of the fumaroles in La Fossa Crater, as well as the variations in their chemical composition, alarmed the scientific community. During that period, in the city of Palermo, Marcello Carapezza along with his colleagues Mariano Valenza and Mario Nuccio, were studying the fumarolic field of Vulcano. After extended bibliographic research, Valenza discovered the studies of Ludovico Sicardi, which were focused on Vulcano, Stromboli, Vesuvio and Campi Flegrei. Considering the fact that Sicardi's research was performed 60 years before its discovery, the scientists decided to meet Sicardi and discuss about his innovative work. They arrived late though; Ludovico had passed away a month before. Carapezza contacted Sicardi's wife, Zoe, and along with Valenza, went to Sanremo to Sicardi's house. Zoe provided them with information about his life and suspiciously gave them several boxes containing the scientific material of her husband.

Ludovico Sicardi was a chemist and a pharmacist, who was passionate about volcanoes. During his several field trips in Vulcano, he observed and described the fumarolic field on systematic basis, measuring the temperatures and recording their variations over time (Sicardi, 1973). He also performed the first chemical analysis of fluids emitted by fumaroles in Vulcano Island and Solfatara. Furthermore, he was the first to hypothesize the coexistence of SO<sub>2</sub> and H2S in fumarolic discharges, which by that time was considered impossible. Also, he succeeded in measuring their ratio by developing an in situ method that chemically separated the S-gaseous species. This method was based on the sampling of fumarolic fluids, using a glass flask that contained a NH4OH-AgNO3 solution, with the aim to dissolve the soluble acid gases ( $CO_2$ ,  $SO_2$  and HCI) and block H2S as an insoluble Ag2S (Sicardi, 1955). Based on his articles, Sicardi can be considered as a precursor of the modern volcanic monitoring.

The scientific material of Sicardi was well preserved in Valenza's office and returned to light thirty-five years later, on the 20th of April 2018. This precious material was donated to the Museum of Mineralogy of Palermo and it is nowadays subject of study and cataloging by the collaborators of the Associazione Geode. The donation consists of his scientific field-equipment, glassware, copies of the scientific articles, old maps, photos of Vulcano and Solfatara. Among these, several notes and three important unpublished researches about Vulcano, Vesuvio and Campi Flegrei were found.

Sicardi, L. (1955): Captazione ed analisi chimica dei gas della esalazione solfidrico-solforosa dei vulcani in fase solfatarica. Bull. Volcanologique, ss.II t.17, 107-112.

Sicardi, L. (1973): The thermal oscillations of the fumaroles of the Island of Vulcano from 1913 to 1970. Stromboli, n.13.

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## Can a simple lherzolitic mantle source explain the geochemical variation of Etnean magmas through time?

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Keywords: Mt. Etna, Mantle sources, Hyblean.

The petrological features of the mantle beneath Mt. Etna is a controversial topic. The lack of erupted primary magmas and mantle xenoliths prevent any direct or indirect evidence of its nature and melting or metasomatic processes. The proximity of Mt. Etna to the Ionian slab and the time-related evolution of its magmatic products introduce further difficulties. On the contrary the nearby Hyblean Plateau provide large amount of mantle xenoliths and primitive products. A petrological comparison highlights several similarities similarity between the two districts, paving the way to the hypothesis that a similar mantle source could be responsible for the generation of both Etnean and Hyblean magmatisms. A detailed mass balance calculation allowed to reconstruct Mt. Etna primary magmas from the initial tholeiitic episode to the post-1971 (nowadays) stage. This simulation consisted of a backward fractionation process, in which olivine and clinopyroxene in progressive equilibrium were added to the least evolved compositions until the mantle equilibrium condition was reached (Mg# 68 of the melt, Fo<sub>ss</sub> in olivine). A second step was then performed to reconstruct the fertile mantle source, using mineral compositions of the Hyblean mantle xenoliths, plus amphibole from Antarctica. According to our simulation, a homogeneous lherzolitic mantle melted at various degree from 10 to19% is able to reproduce the entire range of Etnean lavas, including the post-1971 products. In our modelling, the K and LILE enrichment of post-1971 magmas can be simply related to the variation of the amphibole and phlogopite melting proportions, whose stability is in turn linked to the activity of H<sub>2</sub>O and CO<sub>2</sub> of the system. A geodynamic model for the evolution of this portion of the Eastern Sicily is also taken into account to explain the fairly homogeneous composition of the Etnean magmas, indirectly reinforcing our petrological reasoning.

## Crystallization of an alkali-granitic enclave from a pantelleritic ignimbrite from Pantelleria, Italy

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Keywords: peralkaline magmatism, mineral stability, Pantelleria.

Granular enclaves of alkali-granitic composition are peculiar components in a peralkaline low aspect ratio ignimbrite at Pantelleria and have been indicated as possibly documenting the onset of the magmatic activity at the island. An  ${}^{39}$ Ar- ${}^{40}$ Ar age of 517±19 ka has been in fact obtained for these rocks (Rotolo & Villa, 2001), which predates the eruption of the older pantelleritic magmas by c. 200 ka. The enclaves are particularly abundant at the base of the ignimbrite, as clasts of lapilli to block size in eutaxitic massive lapilli-tuff. New preliminary petrological investigations indicate a heterogranular medium-fine grained texture with some larger alkali feldspar and quartz. The mineral assemblage consists of alkali feldspar (50 vol. %), quartz (30 vol %), Na-pyroxene (10 vol %.), Na-rich amphibole (7 vol. %) and oxides (3 vol. %). According to microstructural relationships, pyroxene was the first crystallizing phase, followed by alkali feldspar and amphibole. However, amphibole locally occurs as corroded relict inside the pyroxene. Pyroxene and amphibole stability appears therefore alternated, possibly reflecting variations of P, T, fO,, aH,O, conditions ascribable to the entrainment of the enclave in the ascending peralkaline magma that originated the pyroclastic density current. In fact, the associated temperature increase and rapid decompression (and related increase in aH<sub>2</sub>O) could have induced some remelting in the enclave, as also suggested by disequilibrium microstructures exhibited by quartz and feldspar crystals in the granite enclave. Data from experimental phase equilibria for compositionally similar effusive pantellerites (Di Carlo et al., 2010) indicate clinopyroxene as liquidus phase, followed by alkali feldspar and then by quartz. Phase assemblages dominated by feldspar, clinopyroxene and aenigmatite would correspond to magma chamber crystallization at P of c.  $120\pm20$  MPa and T of c.  $730\pm10$  °C, with H<sub>2</sub>O<sub>melt</sub> around 4 wt %. Amphibole occurrence, as observed in the studied enclave, appears instead to require higher water contents and lower temperatures (c. 680 °C) and possibly reflect derivation from a deeper and waterricher portion of the reservoir. This work is meant as a starting point for an in depth petrological study of the microgranitic enclaves hosted by the pantelleritic ignimbrites, with the final purpose of achieving a better knowledge of the intratelluric dynamics under a peralkaline volcano that continuously alternated highly explosive ignimbrite-forming eruptions to lower energy explosive eruptions and pantellerite lava flows.

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## Preliminary petrographic and volcanological study of "Punta Karuscia-Punta Spadillo" submerged area, Pantelleria Island (Strait of Sicily)

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Keywords: Submarine volcanic rocks, land sea volcanic correlation, multibeam bathymetry.

The Pantelleria Island (Mediterranean Sea, Italy) is located in the Sicily Channel Rift Zone (SCRZ) and represents the emergent tip of an underwater volcano complex with 72% lying below sea level, down to a depth of about 1200 m. Its origin is linked to the Pantelleria graben, one of the three main tectonic depressions of the NW-SE trending extensional area SCRZ. The rifting process is active since the Late Miocene and was accompanied by a widespread volcanic activity mainly concentrated on Pantelleria and Linosa islands. The volcanic history of Pantelleria started before 320 ka BP and the volcanic activity was characterized by large explosive events, sometimes followed by caldera collapses, alternated to mild eruptions. The last caldera collapse event (45-50 ka BP) followed the major eruption emplacing the Green Tuff ignimbrite. While the post Green Tuff activity has been reconstructed in detail and subdivided into six silicic cycles (pantellerite to trachytes), interposed with mildly alkaline basalts in the NW sector of the island, the volcanic history of Pantelleria before 50 ka BP is poorly known due to the paucity of rock outcrops.

High resolution multibeam bathymetry data (Bosman et al., 2011) show how the volcanic Island rises from a gently sloping seafloor in the NW and in the SE sectors, while is bounded by steep flanks and rimmed by a very narrow or absent shelf on the NW and SW sectors. The definition of the extents and characters of submarine portions of the edifice allow a better comprehension of their structure (Conte et al., 2014). Thus, aimed to provide a contribution in the reconstruction of the evolution of the Pantelleria volcanism, thirteen volcanic rocks were collected in shallow-water, offshore the N-W Pantelleria by SCUBA diving. The rocky outcrops were identified by high resolution multibeam bathymetry data in very shallow water. Preliminary data indicate that the collected samples are variably porphyritic lavas (P.I. = 5-20 % vol) classified as pantellerites and basalt/hawaiites, which features are correlated with those of the emerged area, allowing to outline a preliminary volcanological-map of the submerged sector "Punta Karuscia-Punta Spadillo" of Pantelleria Island in shallow water.

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#### Effect of water on the deep crystallisation of magmas

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Keywords: Hydrous mantle basalts, high pressure storage and differentiation, orogenic settings.

Differentiation of hydrous, mantle-derived basalts is a fundamental process to generate intermediate to SiO<sub>2</sub>-rich products commonly erupted in orogenic settings. The stratigraphic architecture of the crust encountered by primary magma en route to surface dictates how and where differentiation acts. The most important density trap that primarily constrains cooling and crystallisation of primitive magmas is likely located at the mantle-crust transition (i.e., Mohorovičić discontinuity), where high pressure conditions may prevent water loss, thus promoting magmatic differentiation at hydrous conditions. The geochemical signal recorded in the rocks could be strongly dependent on such crystallization conditions. For example, the study of the high pressure basaltic enclaves occurring in the Oligocene andesites of Sardinia indicate that the plagioclase/ melt distribution coefficient of Sr increase by a factor of about 50% for each increase of 1 wt.% H<sub>2</sub>O in the primitive arc magmas. The crystallization at the crust base and hydrous conditions is a process that could contribute to the geochemical signal of the Campi Flegrei magmas. For example, the Na<sub>2</sub>O/K<sub>2</sub>O ratio varies from ~2 to ~0.2 with no clear correlation with the MgO content (2≤MgO≤6 wt.%) in the Campi Flegrei magmas. Such a significant alkali variation cannot be explained by a mere crystal fractionation process in closed system, but it can be more correctly related to an increase of H<sub>2</sub>O in the system. Experiments at 800 MPa and different initial water contents ( $1 \le H_2O \le 6 \text{ wt.}\%$ ) on the primitive alkaline (Na<sub>2</sub>O+K<sub>2</sub>O = 4.32 wt.%) basalts of Campi Flegrei confirm the fundamental role played by water content on the liquidus phases (i.e. clinopyroxene vs clinopyroxene+olivine). However, the change of liquidus phases alone does not explain the TAS differentiation trends shown by the experimental melts at different water contents. In particular, the experimental subalkaline glasses produced under hydrous conditions (4≤H<sub>2</sub>O<sub>i</sub>≤6 wt.%) cannot be explained invoking a closed melt+crystal system. The low alkali content (Na<sub>2</sub>O+K<sub>2</sub>O =1.48 and 3.26 wt.% at 1050°C and 1000°C, respectively) characterising these experiments is inconsistent with the abundance of crystals (clinopyroxene+olivine+orthopyroxene±amphibole±spinel) in equilibrium with the melt. The occurrence of bubbles and halite in these hydrous charges indicates that melt and crystals were in equilibrium with free aqueous fluid phase and that alkali were distributed in the coexisting phases (fluid+melt+crystal). These experimental results and the Na<sub>2</sub>O/K<sub>2</sub>O ratio variability could indicate that the Campi Flegrei magmatic system is characterised by a relatively early and deep degassing process able to remove different proportion of Na and K from the melt.

### Mt. Etna feeding system as deduced by thermobarometric constrains: state of art and future perspectives

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Keywords: Feeding system, thermobarometry, crystal zoning.

The articulated magmatic feeding system of Mt. Etna, characterized by a central open-conduit, three lateral rift systems (NE Rift, S Rift and W Rift) and eccentric, or so called "flank", eruptions represents an almost unique site where to investigate how physical-chemical intensive and extensive variables (P, T, fO,, XH,O) constraint the dynamic of magma ascent, mixing and eruption. In the last decade, several efforts were made to decipher how phenocrysts can record changes in the chemical and physical parameter of the system through compositional and textural zoning. Thermobarometric studies highlighted that during magmatic crystallization along the cotectic Ol-Cpx-Plag, phenocrysts record a continuous crystallization path from mantle depth at almost liquidus temperature (1580 MPa; 1260°C) throughout the crust where mixing frequently involve two main magmatic end members: i) a basic basaltic magma characterized by Ol+Cpx and ii) a trachybasaltic magma involved in massive Plag crystallization. The net effect of this very dynamic feeding system is a mix of phenocrysts with different composition equilibrated with distinct melt compositions, rarely with their host magma. A recent study of the 2011-2012 eruptive events (Giacomoni et al., 2018) suggest that the observed compositional disequilibrium and zoning reflects gradual changes in the P-T conditions and H<sub>2</sub>O content of the crystallizing magma volume, resulting in phenocrysts equilibration within four recurrent physical-chemical conditions asset, defined as "magmatic facies": F1, T=1260°Ca and P>1600 MPa; F2, T=1151-1178°C and P= 600-800 MPa; F3, T=1118-1139°C and P=250-450 MPa and F4, T£1120 °C and P<300 MPa. The coexistence of phenocrysts equilibrated in different magmatic facies in products from temporally close-related eruptive events indicates a dynamic continuous magmatic system, characterized by a vertical zoning in P, T and H<sub>2</sub>O content gradients leading to crystallization of phenocrysts equilibrated at different conditions. This model is apparently in contrast with the view of a feeding system characterized by isolated horizontally extended magma batches, located at different depth (Kahl et al., 2011 and 2015), suggesting that despite the potential useful of this kind of petrographic study, many aspect of the geometry of Mt. Etna feeding system are still unknown.

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#### Effects of variable cooling rates on crystal-chemistry of solidified phases from a basaltic melt

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Keywords: crystal chemistry, MORB, kinetics.

Tholeiitic MORB are the most abundant lavas on the Earth surface, emplaced at near liquidus T; their texture and crystal-chemical attributes are largely influenced by the kinetics of solidification induced by cooling. Despite the importance of these processes, there are still a few experimental studies. Moreover, the investigated thermal ranges and cooling rates are limited. Here, dynamic solidification experiments were designed based on 2D numerical purely conductive cooling simulations of basaltic lavas with variable thickness from 0.1 to several meters. An Icelandic basalt was used as starting glassy material, labelled B<sub>100</sub> glass, with H<sub>2</sub>O < 400 ppm and CO<sub>2</sub>-free. Each solidification experiment was run at P and fO<sub>2</sub> of air, by heating the B<sub>100</sub> glass up to 1300 °C with a rate of 420°C/h. After 2 h at 1300°C, cooling rates (CR) of 1, 7, 60, 180, 1800 and 9000°C/h were applied down to 800°C (quenching temperature). The runs at 1 and 180°C/h were also replicated to verify reproducibility (Vetere et al., 2015).

The identified phases by BS-SEM microphotographs are: clinopyroxene (cpx), plagioclase (plg), spinel (sp) and glass (gl); their area% was measured by image analysis. As CR increases the amount of plg decreases, approaching to 0 area% at CR  $\geq$  180°C/h. Cpx follows an antisymmetric gaussian trend with a tail at CR £ 60°C/h. Sp is invariably < 5 area%. Gl strongly increases from 180 to 9000° C/h. Dendritic textures are observable at CR  $\geq$  180°C/h.

Micro-chemical features were measured either with EPMA-WDS and SEM-EDS. As CR increases, it is found that 1) Si and Fe contents in cpx remain almost constant, while Ca and Mg decrease and Al and  $Fe^{2+}/Fe^{3+}$  ratio almost monotonically increase, 2) Al in sp increases, whereas the concentration of Ti is significant only at 1 °C/h and 3) intriguingly, Al in plg decreases with increasing CR showing an opposite trend relative to that generally documented at disequilibrium crystallization conditions. This is mostly controlled by the proportions of the crystallizing minerals, rather than kinetic effects.

The thermal range and cooling rates investigated here are the widest experimentally reproduced so far. They thus can overall mirror solidification conditions of basaltic melts with variable thickness and distances from air and/or seawater contacts. Heat loss simulations indicate that some m-thick basaltic lavas have interior parts solidifying at CR of 1 and 7° C/h, whereas the outermost portions (< 1 m) experience CR up to 9000° C/h. Finally, Al<sup>3+</sup> is the key element to track kinetics conditions and, possibly, to calibrate efficient geospeedometers.

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# Crystallization of K-feldspar megacrysts in a molten system: evidence from the two-mica porphyritic granitoids of Capo Vaticano Promontory (Serre Batholith, southern Italy)

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Keywords: Rheological lockup threshold, Granodiorite-Granite, central Calabria.

K-feldspar megacrysts (>5 cm in lenght) in granitic rocks have been traditionally defined as early grown in a predominantly molten system, below the rheological lockup treshold (c. 0.5 crystal fraction; e.g., Vernon & Paterson, 2008). Recent studies, starting from the observation that K-feldspar phenocrysts >4 cm are exceedingly rare in compositionally similar volcanic rocks, have questioned this hypothesis (e.g., Glazner & Johnson, 2013). These studies attribute the megacryst growth to late-stage textural coarsening caused by thermal cycling, that would remelt smaller crystals, providing material for the growth of more thermodynamically favorable larger crystals. The present study was carried out by field investigations of two-mica porphyritic granodiorites and granites cropping out in the Capo Vaticano Promontory (central Calabria). These granitoids, representing a deep-intermediate level of the late Variscan Serre Batholith (e.g., Caggianelli et al., 2000; Fiannacca et al., 2017), are characterised by K-feldspar megacrysts up to 12 cm long (e.g, Del Moro et al., 1994). This study was aimed to identify the crystallization and growth time of the megacrysts in relationship to the rheological lockup treshold, by analyzing spatial distribution of the megacrysts in terms of abundance and size, as well as the megacryst-megacryst and megacryst-matrix relationships in the outcropping rocks. The field survey highlighted the presence of a number of relevant features such as: flow structures given by megacryst alignment with no associated deformation; megacryst mechanical accumulations, poikilitic texture with zonal arrangement of the included mineral phases; simple twinning; crystal sinneusis; evidence for filter press process at the interface between the porphyric granitoids and the underlying tonalitic rocks. All these features are diagnostic of early crystallization and growth of the megacrysts in a dominantly molten system, and some of them also reflect free movement of the crystals in the magma, therefore indicating that K-feldspar can achieve their large final size below the rheological lockup threshold.

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#### Solidification of silicate melts: an experimental perspective

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Keywords: solidification, nucleation, crystal growth silicate liquids magmas.

The transition of a silicate liquid to a solid is complex and strongly dependent on thermal (*T*) and temporal (*t*) variations. The *T*-*t* path of a bulk system may control compositions and textures of phases. However, the effect of similar  $\hat{a}^{\dagger}T/\hat{a}^{\dagger}t$  on variable bulk composition *X* is lacking, as well only a limited range of  $\hat{a}^{\dagger}T/\hat{a}^{\dagger}t$  have been investigated.

In this study, a sub-alkaline compositional join has been investigated using six glassy materials  $(H_2O < 500 \text{ ppm})$  with X from basalt- $B_{100}$  to rhyolite- $R_{100}$ , including  $B_{80}R_{20}$ ,  $B_{60}R_{40}$ ,  $B_{40}R_{60}$  and  $B_{20}R_{80}$  intermediate compositions. These glasses have been re-melted at 1300 °C and air conditions (super-*liquidus*) for 2 hours and then cooled at 9000, 1800, 180, 60, 7, and 1 °C/h down to 800 °C. This resulting run-products have been analyzed with about 400 BS-SEM microphotographs and then treated by image analysis to quantify the textural changes. The cooling rate able to crystallize 2 area% of crystals has been used to determine the critical cooling rate *Rc*, i.e. the lowest rate to impedes nucleation.

From basalt to rhyolite, *Rc* changes over 5 orders of magnitude, following a sigmoid path.  $B_{100}$ ,  $B_{80}R_{20}$ ,  $B_{60}R_{40}$ ,  $B_{40}R_{60}$ ,  $B_{20}R_{80}$  and  $R_{100}$  have *Rc* of 9000, 8020, 3020, 620, 7 and < 1 °C/h, respectively. SiO<sub>2</sub> or NBO/T *versus Rc* sigmoid trends hold also for latitic and trachytic *X*. At a fixed *X*, the amount of crystals decreases as a function of cooling rate; however, this trend is not always monotonic, since plateau and even irregular behaviour are observed.

 $B_{100}$  is the silicate melt most prone to nucleate, being highly crystallized between 1 and 60 °C/h and still crystal-rich at 180 and 1800 °C/h. Therefore, this *X* offers the most valuable and expanded investigations for textural changes, as well as for crystal-chemical attributes of plg, cpx and sp (see Giuliani et al. here). Faceted to dendritic textures switches between 60 and 180 °C/h. Sp is  $\leq$  5 area%, cpx content displays a very broad and asymmetric fan with a long tail at low cooling rates and and plg is suppressed at 60 and 180 °C/h, but is able to grow up to 1 mm at 1 °C/h. As the cooling rate increases, CSD curves constantly shift upward, became steep and large crystal sizes disappear, for all crystal type. The maximum and average crystal growth rates (by CSD) increase with increasing cooling rates. A basaltic melt is thus able to broadly change its paragenesis and textures only in response of variable cooling rates.

#### Marsilian explosive phenomena investigated by analysis of proximal and distal deposits

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Keywords: Marsili, tephras, explosive eruptions.

The Marsili seamount has been cored at two different sites that are at a distance of 942 m. The cores are named CORE02 (839 b.s.l.) and Marsili1 (943 m b.s.l.). CORE02 hosts TEPH01 (15 cm) and TEPH02 ( $\geq 60$  cm) tephra layers, emplaced about 3 and 5 ky B.P. and characterized by similar compositions and petrography. Conversely, Marsili1 hosts five tephras with thickness of only a few cm. TEPH01 and TEPH02 show either fall- and flow-like pyroclastic features, while the Marsili1 shows only the fall-like pyroclastic feature (Iezzi et al., 2014; Tamburino et al., 2015). In this study we investigate the textural and morphological features of minerals, bubbles and ash grains in 13 and 6 samples from CORE02 and Marsili1 logs, respectively, employing 2D techniques and phase-contrast synchrotron X-ray computed microtomography.

The size of pumices of the two uppermost tephras decreases from CORE02 to Marsili1, whereas bubbles range between 5 and 40 vol.%. High similarities of glass compositions, ages and 3D textures of bubbles indicate that the two shallowest pyroclastic layers are proximal and distal counterparts of two submarine explosive eruptions. FTIR measurements conducted on these two shallowest deposits indicates  $H_2O$  and  $CO_2$  concentrations in the glass < 1 and ~0 wt.%, respectively. Numerical simulations performed using solubility models, by modulating *T*, *P*, and  $H_2O$  amount in the system for both TEPH01 and TEPH02, suggest that the gas to magma ratio, admitting that outgassing is impeded, requires at least 3 wt.%  $H_2O$  to attain a nominal fragmentation threshold of 80:20 (gas:liquid). The low amounts of measured bubbles and dissolved  $H_2O$  evidence that a large part of bubbles was not recorded. This scenario agrees with the occurrence of cm-sized bubble walls on the external surfaces of pumices (i.e. elliptical shadows) that can be captured only by 3D images.

The Marsili seamount thus erupted explosively in the last thousand of years, forming both fall- and flowlike deposits, dispersed in an area of some km<sup>2</sup> However, submarine currents could have enhanced these dispersions. The studied scorias and ash can be referered to a "Marsilian" eruptions, since proximal and distal explosive sub-marine fall deposits, flow-like and erosive horizons, as well as a such very low amount of bubbles in a tephra have never been documented in literature.

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#### Synchrotron X-ray microtomography for a 3D characterization of pyroclastic products from the 1538 AD Monte Nuovo eruption (Campi Flegrei, Italy)

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Keywords: X-ray micro tomography, Synchrotron, Monte Nuovo.

X-ray computed microtomography (XmCT) is a well-know technique for non-destructive analysis of internal features of various types of samples both in life and materials science applications. The information achievable by XmCT is not limited to a qualitative volume inspection but, through image processing analysis, a three-dimensional (3D) quantitative description becomes available for modeling and further interpretations. The interest to XmCT in volcanology increased thanks to the possibility to obtain the 3D visualization of morphological and textural features in pumices or scoriae samples, combined with a quantitative evaluation of important parameters such as porosity, density, connectivity and tortuosity.

In this work, phase=contrast synchrotron XmCT has been applied to investigate a set of samples representing the complete stratigraphic sequence of Monte Nuovo eruption (1538, Phlegrean Fields, Italy). Data have been acquired at the SYRMEP beamline of the Elettra synchrotron facility, (Trieste, Italy) and further processed by using the custom-developed software *Pore3D* (Brun et al., 2010) for the feature analysis.

Monte Nuovo eruption has a strategic significance in the framework of volcanology and volcanic hazard because (1) it represents the last historical explosive emission of this strongly populated area, and (2) its volcanic evolution is well-known being described by eyewitnesses (Di Vito et al., 1987; Lirer et al., 1987). Several works on this eruption or in the surrounding area (Piochi et al., 2005, Polacci et al., 2006; Polacci et al., 2014) are available in the literature, based on XmCT or conventional techniques (optical and SEM microscopies) thus providing a useful data set for comparison.

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#### Extremely fast magma dynamics at Mt. Etna revealed by clinopyroxene growth

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Keywords: Etna, clinopyroxene, undercooling.

Mt. Etna is one of the most active volcanoes in the world. The broadly constant composition of magmas erupted and the compositional zoning of minerals suggest a dynamic plumbing system, in which magmas ascent, cool and crystallize in relatively short time scales (months to years). However, in order to correctly decipher the time scales of eruptions, the kinetic effects driving the crystallization must be carefully investigated and evaluated. To this purpose, we present dynamic crystallization experiments carried out on one of the most primitive trachybasalt (SiO<sub>2</sub>= 48 wt.%, Na<sub>2</sub>O+K<sub>2</sub>O = 4 wt.% and MgO = 8 wt.%) from Mt. Etna (Italy) and designed to quantify the effect of undercooling ( $\Delta T = T_{liquidus} - T_{crystallization}$ ) on hydrous and anhydrous magma storage (P = 300-800 MPa) conditions. Differently from classic isothermal experiments, dynamic experiments were heated at temperatures above the liquidus (1300 °C) and cooled down to the final target temperature at a constant rate (80 °C/minute). Clinopyroxene and titanomagnetite are the dominant mineral phases. Plagioclase crystallizes only under anhydrous conditions, whereas amphibole forms in hydrous experiments equilibrated at 800 MPa. Olivine appears only at 300 MPa under isothermal conditions. Clinopyroxene growth rates are maximum at very low degrees of undercooling ( $\Delta T \le 20$  °C), producing exceptionally large euhedral crystals (>500  $\mu$ m). In contrast, at moderate to high degrees of undercooling ( $\Delta$ T>20 °C), skeletal crystal shapes prevail. Growth rates from undercooling experiments are orders of magnitude higher than those from isothermal experiments, where smaller (<50 µm) euhedral minerals occurs clustered in crystal patches. Compositional sector zoning of clinopyroxene is observed at high degrees of undercooling ( $\Delta T > 50^{\circ}$ C), accounting for a very fast (few minutes) growth of skeletal crystals followed by a slower (few hours) filling and coarsening of crystal mantle and rim. Undercooling experiments closely reproduce the compositions of magmas at Mt. Etna and set constrains on magma evolution and dynamics, indicating early crystallization of clinopyroxene  $\pm$  amphibole at P = 800-400 MPa, followed by late crystallization of plagioclase and olivine at P <400 MPa. The water content in magmas never exceeding 2 wt.% and the extremely fast crystal growth rates by the undercooling remark the development of open-system conduit processes related to extremely fast dynamics (i.e., ascent, crystallization and eruption) of magmas erupted at Mt. Etna.

#### The evolution of the cenozoic alkali basalts, SW Poland

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Keywords: Basanites Mantle, potential temperature, Plumes.

Cenozoic lava flows and necks belonging to the Central European Volcanic Province are widespread in Lower Silesia in SW Poland. They occur in the NE part of the Variscan Bohemian Massif. Part of the lavas occurs at the NE prolongation of the Ohře (Eger) Rift into Poland, whereas those situated in the central and eastern parts of Lower Silesia are distant from the Rift. Samples from 22 outcrops show that, besides one site consisting of basaltic trachyandesites, the majority of the lavas are nephelinites and basanites, with eruption ages ranging from 31 to 4.5 Ma ago.

The nephelinites and basanites have Mg# varying from 54 to 63 and from 62 to 71 respectively. They have low total alkalis that range from 3.5 to 6.3 wt% and Ba/Ce ratios that vary between 4.5 and 6.5, which are consistent with the mean OIB ratio of 4.5. The radiogenic Sr and Nd isotopic ratios have values similar to DMM (0.703115-0.703867 and 0.512780-0.513015 respectively)

The calculated melt segregation temperatures for basanites range between 1550 and 1580 °C (Herzberg & Asimow 2008), which correspond mantle potential temperatures around 1480 °C that is higher than the mantle ambient temperature estimated to be 1400 °C. Pressure estimates for the segregated melts are 3 GPa, which correspond depths of approximately 100 km (Scarrow & Cox, 1995).

The estimated high Mantle Potential T point to a thermal anomaly underneath the studied area, which coincides with the postulated low-velocity material underneath Europe (Hoernle et al. 1995). This could be attributed to local small "finger-like" plume activity causing alkaline volcanism (Granet et al., 1995). However not everywhere in Europe the alkali basalts are related to plumes. Ali and Ntaflos, 2011 have shown that in Styrian Basin, Austria, the mantle potential temperature is below 1400 °C and that lithospheric attenuation is responsible for the generation of the alkali basalts. It is therefore evident that thermal anomalies are not widespread everywhere underneath Europe but there are small low-velocity bodies causing the alkaline volcanism. This could be valid at least for SW Poland.

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### Comprehensive model for Na- and K- diffusion in alkali feldspar

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Keywords: sanidine, alkali diffusion, diffusion model.

Sanidine, a widespread phase in K-rich volcanic rocks, may be regarded as an essentially binary solidsolution between KAlSi<sub>3</sub>O<sub>8</sub> (Ksp) and NaAlSi<sub>3</sub>O<sub>8</sub> (Ab). Whereas Si and Al are strongly bound in the silicate framework, the alkali cations are located in large, irregularly coordinated cavities and less strongly bound. As a consequence, the alkali cations are rather mobile within the crystal structure making sanidine prone to composition change during cooling and mineral-melt interaction. In this context the intracrystalline diffusion of Na<sup>+</sup> and K<sup>+</sup> is of pivotal importance. Na-K interdiffusion experiments (Petrishcheva et al, 2014) revealed considerable diffusion anisotropy with D<sub>NaK</sub>[001] approx.  $10xD_{NaK}$  [010]. In contrast, more recent radiotracer experiments using oriented single crystals of alkali feldspar combined with the sectioning method (Hergemöller et al, 2017) indicate no or minor anisotropy of Na<sup>+</sup> and K<sup>+</sup> tracer (self) diffusion. The apparent discrepancy between interdiffusion- and radio-tracer experiments is probably due to the inherent complexity of interdiffusion resulting from potential thermodynamic and mechanical effects. This calls for a new approach for analysing complex diffusion in alkali feldspar. Combined tracer-diffusion and interdiffusion experiments are underway, whereby oriented plates of gem-quality sanidine and 95% <sup>41</sup>K enriched KCl salt melt are used as diffusion couples. Concentration-distance data for Na, <sup>39</sup>K, and <sup>41</sup>K are available from TOF-SIMS depth profiling.

We developed a new diffusion model, which accounts for vacancy-mediated self-diffusion and for binary exchange of  $Na^+$  and  $K^+$  by means of site swapping. The transport processes are analysed theoretically by numerical solution of coupled diffusion equations for the three species Na, <sup>39</sup>K, and <sup>41</sup>K. The model equations are derived in the most general form combining the free energy approach and Onsager's reciprocal relations. The diffusion equations for the individual species are nonlinear, where in our model, the nonlinearity is derived analytically from first principles. Numerical solutions of the coupled diffusion coefficients and the diffusivity resulting from the binary exchange by site swapping. The resulting coefficients are in reasonable agreement with those published by other authors and have a clear physical meaning.

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# Experimental constraints on pre-eruptive conditions of a chemically zoned peralkaline reservoir: the example of Green Tuff eruption at Pantelleria (Italy)

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Keywords: Phase equilibria, peralkaline magmas, Pantelleria.

The Green Tuff eruptions of Pantelleria is the sole known compositionally zoned ignimbrite at this volcanic location, whose composition varies from a crystal-poor pantellerite at the base towards a crystal-rich trachyte at the top of the eruptive sequence. Here, we present the results of a series of crystallization experiments performed on starting materials representative of the bottom and top of the eruptive sequence. Experiments were performed in the temperature range 750-950°C, pressure 1-1.5 kbar, fluid saturation conditions with  $XH_2O$  (=H\_2O/H\_2O+CO\_2) between 0 and 1 and redox conditions fixed around the FMQ buffer. Results show that at temperature of 900 °C pantelleritic starting compositions are well above their liquidus regardless their water content, while in trachytes at 900°C are stable clinopyroxene, Fe-rich olivine and alkali feldspar (Romano et al., 2018). This latter becomes the most abundant mineral phase (up to 80 wt%) when temperature and melt water content decreases, while the proportion of mafic phases is never above the 10wt%. In the experiments performed on pantelleritic starting material (at T= 750  $^{\circ}$ C) the equilibrium mineral assemblage is clinopryxone, alkali feldspar, quartz as well as fayalite and aenigmatite. In particular, the relationship between these latter two mineral phases appears controlled by melt peralkalinity and redox conditions confirming the results of White et al. (2005) for natural pantellerites, never verified experimentally (Di Carlo et al., 2010). Experiments reproduced the mineral assemblages of the natural rocks, constraining the pre-eruptive pressure at  $P \sim 1$  kbar and highlighting that the compositional zoning in magma chamber (trachyte to pantellerite) is related to a temperature gradient (750°C-900°) within the reservoir. Moreover, our results allow demonstrating that a peralkaline liquid derivate can be produced from a metaluminous trachyte at T<  $850^{\circ}$ C after extensive alkali feldspar crystallization (~ 80 wt%).

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# Volatiles and trace elements in melt inclusions from the zoned Green Tuff ignimbrite, Pantelleria

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Keywords: Melt inclusions, Pantelleria.

The Green Tuff (GT) ignimbrite, erupted at Pantelleria (Sicily) ca. 45.7 +/- 1.0 ka ago, represents a good example of dynamics of low-volume ( $\leq 1 \text{ km}^3 \text{ DRE}$ ) chemical zoned peralkaline silicic magma chamber, likely fed by a parental basaltic magma. The GT ignimbrite is zoned from pantellerite at the base to a crystalrich (crystal content >30 vol%) comenditic trachyte at the top, with the pantellertic compositions dominating on the whole erupted volume. We present here new data on melt inclusions (MIs) from the pantellerite and trachyte portions of the GT eruption. We document the first occurrence of trachytic melt inclusions in the lateerupted member, whose importance resides in the fact that trachytes were known mostly as crystal-rich lavas or ignimbrites, all variably affected by crystal accumulation. Trace elements compositions of MIs highlight the occurrence of two types of trachytic melts: (i) a low-Ba melt, directly descending from basaltic melts by 60-70 % of fractional crystallisation, and (ii) a high-Ba melt that might be affected by processes of feldspar dissolution, small-scale mixing and entrainment of the resulting melts in some MIs. Volatile contents of MIs from the whole Green Tuff sequence reflect an -H<sub>2</sub>O-rich top magma chamber ( $\leq 4.2$  wt % in the early tapped pantellerite portions) grading in an H<sub>2</sub>O-poor bottom ( $\leq 1.2$  wt % in the late erupted crystal-rich trachyte), suggesting either that trachyte magma was H<sub>2</sub>O-undesaturated, or a consistent H<sub>2</sub>O loss from the clinopyroxene hosted melt inclusions. Our results suggest that the comenditic trachyte represented by the melt inclusions may form after ~65% FC of an assemblage dominated by plagioclase and clinopyroxene from an alkali basalt, and that pantellerite is the result of an additional 90% crystallization of an assemblage dominated by alkali feldspar (for a total of ~97% FC of basalt). In this suite, the maximum Ba concentration through fractional crystallization processes is ~1300 ppm. Higher Ba values in trachytes are suggestive of feldspar accumulation or resorption processes.

#### Water solubility in pantelleritic melts

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Keywords: water solubility, pantellerite, experimental petrology.

While there exist abundant data for water solubility in metaluminous (typical calc-alkaline) rhyolitic melt compositions, our knowledge of water solubility in pantellerites (strongly peralkaline rhyolites) remains limited, even though studies of melt inclusions in such magmas show they may be water-rich (Lowenstern & Mahood, 1991; Barclay et al., 1996). To improve our knowledge of water behavior in peralkaline rhyolites we have condicted several series of new experiments at P=50 to 200 MPa and T=800-850°C using a sythetic pantellerite starting composition with (wt%) SiO<sub>2</sub>=76.6, Al<sub>2</sub>O<sub>3</sub>=8.48, FeO\*=5.48, K<sub>2</sub>O=3.68, Na<sub>2</sub>O=4.72, with molar (Na+K)/Al=1.38 Some experiments were H<sub>2</sub>O undersaturated (~2 to 6 wt% H<sub>2</sub>O) and the products of these experiments were analyzed by Karl-Fischer Titration (KFT) for total dissolved H<sub>2</sub>O abundance. The results from these experiments were used to estimate new extinction coefficients for infrared absorption bands at ~4500 cm<sup>-1</sup> and ~5200 cm<sup>-1</sup>, commonly attributed to molecular water and hydroxyl groups, respectively. Preliminary results suggest molar absorptivity values of 1.80 and 1.62 l mol<sup>-1</sup> cm<sup>-1</sup> for the 4500 cm<sup>-1</sup> and 5200 cm<sup>-1</sup> bands, respectively.

Additional water saturated experiments at 50-200 MPa, 850°C demonstrate water solubilities, on a wt% basis, in our pantelleritic composition that are significantly higher than observed H2O solubilities in metaluminous rhyolitic compositions (approximately 1 wt% higher at 100MPa, close to 2 wt% higher at 200 MPa). In addition, trying to calculate H<sub>2</sub>O solubilities using existing models (e.g. Moore et al., 1998; Ghiorso & Gualda, 2015) consistently underestimates solubilities, whereas the recent model of Papale et al. (2006) reproduces our dato within < 0.5 wt%. Current work in progress is attempting to better define observed solubility variation, as well as exploring possibilities to use Raman spectroscopy for total H<sub>2</sub>O measurements on the same glasses we have analyzed using KFT and IR spectroscopy.

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# Experimental measurements of viscosity and melt structure of CO<sub>2</sub>-bearing melts at high pressure and temperature

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*Keywords*: CO<sub>2</sub>-bearing melts, viscosity, melt structure.

 $CO_2$ -rich melts like carbonatitic and kimberlitic magmas are produced at pressures and temperatures of the Earth's upper mantle by low degrees of partial (redox) melting of both carbonated peridotites and eclogites. To date, despite previous studies investigated P-T- $fO_2$  conditions at which these melts can form, we still lack information about their viscosity and structure that strongly influence their rheological properties, i.e. the movement of these magmas from the rock source to the surface.

In this study we investigated viscosity and melt structure of carbonated melts using both synthetic glasses and rock powders for a total of four starting materials with  $SiO_2$  content varying from 0 to ~36 wt% and  $CO_2$  amount from ~40 to 3 wt%.

Such experiments were carried out at pressures of 1-6 GPa and temperatures between 1050 and ~2000 °C using the Paris-Edinburgh press combined with in situ synchrotron X-ray diffraction at beamline 16 BM-B of HPCAT (Advanced Photon Source, Illinois, USA). Viscosity measurements were performed using the *falling sphere* technique. A high-speed camera collecting up to 1000 frames per second recorded the fall of a Pt probing sphere in the molten sample and viscosity was then calculated using the Stokes' equation.

Structural measurements of carbonated melts were performed at high temperature and pressure over 3-4 hours by multi-angle energy dispersive X-ray diffraction technique (2 theta ranging from 3 to 28 degrees).

Our results show viscosity values from less than 0.01 Pa·s for our SiO<sub>2</sub>-free composition, that increase up to two orders of magnitude as we consider melts with 36 wt% SiO<sub>2</sub> We interpret this sharp increase in viscosity as due to SiO<sub>2</sub> polymerization effect. The mobility for the SiO<sub>2</sub>-free and SiO<sub>2</sub>-bearing melt ranges from ~150 g·cm<sup>-3</sup>·Pa<sup>-1</sup>·s<sup>-1</sup> to 1.5 g·cm<sup>-3</sup>·Pa<sup>-1</sup>·s<sup>-1</sup>, calculated at depths of 90-120 km. Mobility in turns influences the migration rate of these melts through upper mantle rocks that, within the same depths, has been estimated to increase from 0.01 to 0.22 km/yr.

In addition, preliminary structural measurements allowed us to determine interatomic distances of the melt at HP-HT. Results for the carbonatitic melt with 5wt% SiO<sub>2</sub> show M-O (M=Ca, Mg, Fe) and M-M distances being ~2.5Å and ~4Å, respectively, similarly to what noticed by Kono et al. (2014) for calcite (Ca-O=2.3Å; Ca-Ca=4.2Å) and dolomite melts (M-O=2.1Å; M-M=3.9Å). On the other hand, melts with 18 wt% and 36 wt% SiO<sub>2</sub> showed M-O distance of 3.3Å and 3.2 Å respectively, constant M-M distance (~4.2Å) and Si-O distance of ~1.7Å.

Results from our study allows the ascent of  $CO_2$ -rich melts to be modelled as function of pressure, temperature and mantle oxidation state with implications for the speciation of carbon from the mantle up to the surface as function of time.

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### The Apacheta-Aguilucho Volcanic Complex (Northern Chile): plumbing system processes through the thickened crust and constraints given by areal distribution of the Altiplano-Puna Magma Body

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Keywords: Continental arcs, magmatic plumbing system, enclaves.

Petrological investigations were performed on the Pliocene-Pleistocene Apacheta-Aguilucho Volcanic Complex (Andean Central Volcanic Zone, Northern Chile) mainly consisting of andesite to rhyolite high-K calcalkaline lavas. In this area the most recent eruptions (<150 ka) of the Chanka, Chac-Inca and Pabellón dacitic domes represent the waning stage of the magmatic flare-up (10-1 Ma) of the Altiplano-Puna Volcanic Complex. This is an ignimbritic plateau extending between Chile, Bolivia and Argentina (21-24°S), characterized by an episodic spatiotemporal pattern of eruptions at rates much higher than those typical of continental arcs.

A model for the evolution of the rising mantle-derived basaltic-andesite magmas through crustal assimilation and fractional crystallization (AFC) is proposed, emphasizing as a potential contaminant the role played by the Altiplano-Puna Magma Body (APMB; 4-25 km below sea level), a huge igneous, partially-molten body with a volume of ca. 500,000 km<sup>3</sup> APMB is an incrementally constructed, upper-crustal batholith where the S-waves velocities are < 2.9 km/s. Fractional crystallization (FC) of the magmas at shallower crustal levels (~4-8 km) is the final stage of differentiation. According to petrological data, the 3D distribution of the APMB seems to influence the degree of crustal assimilation of the erupted magmas: the more the S-waves velocities of this geophysical anomaly decrease (i.e. the inner core of the APMB) the more crustally contaminated the erupted magmas will get (e.g. higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios). This correlation can be distinctively recorded from the volcanoes above the marginal (outer) zones of the APMB (e.g. Ollagüe, La Poruña, Lascar) to the most crustally contaminated magmas erupted from volcanoes built upon the central areas of the APMB (e.g. Uturuncu, Bolivia), passing through the intermediate ones such as the Apacheta-Aguilucho Volcanic Complex and the nearby domes. We also constrained the replenishment of the basic-intermediate melts into the highly porphyritic dacite magma chambers. This kind of plumbing system process was responsible to gas exsolution and quenching of the higher temperature and lower viscosity andesite magma and formation of the microvesiculated enclaves, so widespread in many of the youngest domes of the investigated area. The microvesiculated enclaves of Chanka, Chac-Inca and Pabellón domes well agree with the "model B" of Coombs et al. (2002), which makes possible the coexistence of slight different petrographic (grain size, modal mineralogy, vesicularity) and petrological (e.g. isotope ratios) features of the enclaves independently from their size, as they correspond, before floating into the highly porphyritic dacite, to different distance from the mixing/mingling andesite-dacite interface.

Coombs, M.L., Eichelberger, J.C. & Rutherford, M.J. (2002): Experimental and textural constraints on mafic enclave formation in volcanic rocks. Jour. Volcanol. Geoth. Res., 119, 125-144.

### Plagioclase records variable-H<sub>2</sub>O contents in basaltic to andesitic magmas from Capo Marargiu Volcanic District (Sardinia, Italy)

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Keywords: Plagioclase, Strontium, Trace elements.

Capo Marargiu Volcanic District (CMVD) is an Oligo-Miocene calc-alkaline complex located in northwestern Sardinia (Italy) and characterised by the widespread occurrence of basaltic andesitic to andesitic domes and dikes. These rocks are porphyritic ( $\leq$ 15% of phenocrysts) and mostly consist of submillimetreto millimetre-sized plagioclase, whereas submillimetre-sized pyroxene and titanomagnetite are scarce. One of the domes hosts a multitude of high-Mg basaltic enclaves showing porphyritic (~40-50%) texture, with millimetre- to centimetre-sized clinopyroxene + amphibole + plagioclase + olivine + Cr-spinel (in order of abundance) dispersed in a microcrystalline groundmass of plagioclase + pyroxene + titanomagnetite. In turn, the dikes contain plutonic-textured crystal clots of submillimetre- to centimetre-sized amphibole + plagioclase + titanomagnetite. Based on both bulk-rock data and clinopyroxene + amphibole textural and compositional variations, previous works have demonstrated that enclaves and crystal clots originated by fractional crystallisation of basaltic to basaltic andesitic magmas under lower- to middle-crustal pressures and waterrich conditions. In contrast, the anhydrous paragenesis of basaltic andesitic to andesitic hypabyssal rocks (i.e., domes and dikes) testifies to the ascent and degassing of the more differentiated magma. In this contribution, plagioclase composition is used to investigate the behaviour of volatile components (i.e., H<sub>2</sub>O) during basaltic to andesitic magma differentiation.

Plagioclase composition from enclaves and crystal clots is rather homogeneous, varying within the restricted range of  $An_{77.94}$ . Conversely, plagioclase phenocrysts from domes and dikes show a wide compositional variation, with  $An_{75.95}$  cores grading to  $An_{45.71}$  rims. Sr in plagioclase from all the studied rocks is negatively correlated with An, reflecting both (i) the incompatible behaviour of Sr during magma differentiation and (ii) the higher compatibility of this large cation in the more elastic structure of An-poor plagioclase. Importantly, plagioclase from enclaves and crystal clots show higher Sr (496-910 ppm) than phenocrysts from domes and dikes (342-883 ppm). Using differently calibrated partitioning equations from literature, it is demonstrated that plagioclase from CMVD rocks crystallised from cogenetic magmas with similar Sr-concentration but variable  $H_2O$  contents, with high-Sr crystals belonging to  $H_2O$ -rich magmas. This reflects both (i) the presence of a chemically (i.e.,  $H_2O$ ) zoned magma chamber, and (ii) degassing processes in the CMVD plumbing system. This contribution implies that adopting proper models is crucial to avoid misleading interpretations of magmatic processes.

### The fate of Kfs megacrysts in felsic vs. mafic porphyry magmas

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Keywords: K-feldspar megacryst, Tuscan Magmatic Province, mafic magma.

Mafic and felsic porphyry dykes and laccoliths coexist in the Miocene Tuscan Magmatic Province (Italy), namely at Elba Island and Campiglia Marittima. A striking feature of these porphyries is the presence of cm-sized megacrysts of K-feldspar (Kfs) that include abundant biotite and plagioclase crystals, and minor, quartz and accessory minerals (e.g., zircons, apatite). In felsic porphyries, Kfs megacrysts are euhedral, whereas in mafic porphyries these are characterized by rounded-embayed shapes and reaction zones (Mgenrichment) adjacent to the biotite inclusions, pointing out to disequilibrium processes. A working hypothesis is formulated that the Kfs megacrysts, crystallized in a felsic porphyry magma, were grabbed by the ascending mafic porphyry magma. The different temperature and chemical composition of the mafic magma eventually triggered the reaction textures observed in the Orano mafic dykes (Elba Island) and in the Temperino mafic porphyry (Campiglia Marittima). This work is aimed to experimentally determine the thermo-chemical conditions at which Kfs megacrysts formed in a felsic magma did react in a mafic melt, that are relevant for the emplacing conditions of the two magmas. A euhedral Kfs megacryst was collected from the felsic San Martino porphyry (Elba Island) and the field-emission scanning microscopy images indicate the absence of any reaction zones. Millimetric-size fragments were cut out from across the Carlsbad composition plane of the Kfs and were then encapsulated in 3 mm-outer diameter Au capsules, together with finely ground powder of Orano mafic porphyry. High-temperature experiments were then performed at 1 atm and temperatures between 850 and 1000 °C, using both single Kfs fragments and the encapsulated Kfs cores. First result by fieldemission scanning microscopy indicate that a 5-20 µm thick reaction zone starts formed adjacent to biotite inclusions at temperatures above 850 °C in the encapsulated Kfs cores. The reaction zone at the Kfs-biotite interface reproduces a Mg enrichment similar to that observed in some Kfs from mafic porphyry, constraining a minimum reaction temperature for the emplacement of the porphyry. The results of these experiments are promising for the possibility to infer the physical-chemical conditions at which porphyry magmas intrude in the upper crust.

### Session S21

### Linking deep and surface processes: advances in volcanology from a multidisciplinary perspective

Conveners And Chairpersons Mimmo Palano (INGV, Catania) Antonio Paonita (INGV, Palermo) Matteo Trolese (Università di Roma Tre)

#### Swollen Volcanic Ridges in Pre-Oceanic, Oceanic and Back-Arc Environments

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Keywords: Mid-Ocean Ridges, Anomalous Topograhy, "Swollen Ridges".

Upwelling of the upper mantle below mid-ocean ridges is considered within the theory of Plate Tectonics to be normally a mostly passive process, induced by plate separation along accretionary boundaries. At any given mantle and/or temperature/composition, melt production and crustal thickness depend on rate of upwelling, that is, on spreading rate, resulting in a correlation along ridges of crustal thickness and topographic height with spreading rate (Shen and Forsyth, 1992). Crustal thickness and topographic level vary within a small range in much of the mid-ocean ridge system (Morgan and Chen, 1993). This means that temperature and composition of the upwelling mantle are relatively constant below ridges, except for "hot spots" and "cold spots" regions.

We call attention to a set of anomalous volcanic ridges from different geotectonic settings: an anomalous mid-ocean ridge segment (Spiess Ridge, Southwest Indian Ridge); a back-arc basin ridge (Marsili Ridge, Tyrrhenian Sea); and a "pre-oceanic" rift (the Erta Ale Ridge in the Southern Red Sea rift system). These ridges are more elevated than even those mid-ocean ridge segments that are influenced by "hot spots". A possible qualitative explanation is that these ridges, that we call "swollen ridges", are underlain by upper mantle thermal and/or compositional anomalies producing an unusually high quantity of melt that cannot be accommodated by plate separation. The result is a thicker than normal basaltic crust and an anomalous high topographic level.

Another result of the mantle anomaly that underlies swollen ridges is an unusually shallow subaxial magma chamber, documented particularly for the Marsili and the Erta Ale Ridges. We updated Purdy et al. (1992) curve showing an inverse correlation of subridge magma chamber depth versus spreading rate, confirming the inverse trend between spreading rate and depth of the axial magma chamber. However, our three swollen ridges plot outside the trend, their magma chamber being too shallow for their spreading rate. A qualitative explanation of these observations might be that swollen ridges are created by non-passive processes, whereby the quantity of melt produced by an upper mantle subridge thermal and/or compositional anomaly exceeds the quantity that can be accommodated by plate separation. As a result the thickness of the basaltic crust and the ridge topographic level are higher than normal.

Morgan, P.J. & Chen Y.J. (1993): Dependence of ridge-axis morphology on magma supply and spreading rate. Nature, 364, 706-708.

Purdy, G.M., Kong, L.S.L., Christenson, G.L. & Solomon, S.C. (1992): Relationship between spreading rate and the seismic structure of mid-ocean ridges. Nature, 355, 815-817.

Shen, Y. & Forsyth, D.W. (1992): The Effects of Temperature and Pressure-Dependent Viscosity on Three-Dimensional Passive Flow of the Mantle Beneath a Ridge-Transform System. J. Geophys. Res., 97, 19717-19728.

# Significance and predictive value of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in explosively erupted components of alkaline-mafic pyroclastic deposits

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Keywords: Pyroclastic deposits, fractional crystallization, magmatic modelling.

A fundamental geochemical signature in a high proportion of volcanic rock components is the  $SiO_2/Al_2O_3$  ratio. The process of fractional crystallization at depth causes predictable, systematic differentiation of  $SiO_2/Al_2O_3$  between crystallizing minerals and the accompanying residual melt, as evidenced in lava mineralogy, experimental and theoretical systems. In pyroclastic deposits, fragmented magmatic minerals and glassy components (scoria, pumice, fiammae, shards, melt inclusions) record a range of these  $SiO_2/Al_2O_3$  signatures, including representation of the most evolved residual melt fraction as assessed by petrographic context. When placed into a fractional crystallization framework, the appropriate, analysed melt signature of  $SiO_2/Al_2O_3$  then provides an opportunity to pinpoint magma evolution conditions at depth, immediately prior to explosive eruption.

Surface processes of alteration in the hydrothermal to diagenetic range are also systematic and predictable, most notably for zeolitization of volcanic glass, long established as closely sustaining the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio ( $r^2 = 0.94$  for product-reactant pairs). The relationship therefore presents an opportunity to link zeolitic 'proxyglass' signatures of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> to deep magmatic processes in the same way as for fresh glass, above. The opportunity is important because zeolites typically constitute up to ~80% of components in Italian pyroclastic deposits (Langella et al., 2001), representing substantial proportions of the record of erupted former melts.

In the case of the pervasively zeolitized *Tufo Lionato* deposit of Colli Albani (the caldera-forming Villa Senni eruption), magmatic mineral constituents (leucite, diopside, mica, nepheline) quantified by bulk sample XRD closely match those of the expected fractionating system. The alteration assemblage comprises 42% chabazite, 22% phillipsite, 2.3% analcime, and minor smectite. Proxy-glass  $SiO_2/Al_2O_3$  at 2.05 was determined from 114 microprobe analyses of chabazite and phillipsite. When compared with the whole rock  $SiO_2/Al_2O_3$  signature of 2.68 for the associated pre-caldera lava, the residual melt signature for *Tufo Lionato* is consistent with evolution by magmatic fractionation to a greater extent than evidenced by scarce fresh glass. Reconstruction of this residual melt, its crystallizing minerals and physical parameters at the point of explosive eruption, was enabled by magmatic modelling and successfully validated by comparison with published analyses, especially for clinopyroxene compositions.

Thus, a link from surface processes in deposits to processes and conditions at depth occurring immediately prior to explosive eruption, is not only possible but also uniquely informative, demonstrating the significance and predictive value of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio across disciplines.

Langella, A., Cappelletti, P. & de'Gennaro, R. (2001): Zeolites in closed hydrologic systems. In: Bish, D.L. and Ming, D.W. (eds.) Rev. Min. Geochem. 45, 235-260.

### Microseismicity along the eastern sector of the Provenzana-Pernicana Fault (Mt. Etna, Sicily, Italy)

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Keywords: microseismicity, Provenzana-Pernicana, Mt. Etna volcano.

The Provenzana-Pernicana (PP) fault system is one of the most active tectonic features of Mount Etna. This system, which develops from the Northeast Rift up to the Ionian Sea for a total length of about 18 kilometers, is considered the northern boundary of an unstable sector that includes much of the eastern flank of the volcano. The PP system presents an E-W trend, which appears to be in considerable contrast with the orientation of the main recognizable structural trends in the Etna region. The movement of the structural system PP is allowed to the east by minor faults that together define the Eastern Fault System of Provenzana-Pernicana (EFSPP).

The PP system presents mainly a left lateral kinematics, clearly visible to the west of the village of Presa, near Piedimonte Etneo. In particular, the PP system is seismically active up to the zone of Vena-Presa and is characterized by a seismicity extremely shallow (depth <3 km) with earthquakes that reach magnitude values up to 4.3. Otherwise, the main characteristic of the EFSPP is that the movements are mainly in form of *creep*.

In order to improve the detection capacity of the permanent seismic network, managed by the Istituto Nazionale di Geofisica e Vulcanologia - Osservatorio Etneo - Sezione di Catania - (INGV-OE), the installation of a local seismic network close to the structure it was carried out with the aim to study in detail the low microseismicity of the eastern extension of this fault system.

The mobile seismic network, called *Fiumenet*, has set up since August 2015 between Fiumefreddo and Piedimonte Etneo villages. It consist of six digital stations Nanometrics Taurus, equipped with Lennartz LE-3D 20-s. three-component broadband sensors.

We focused the analyses on a micro-seismic swarm recorded the 4-6 July, 2016 in the area of Vena. The maximum magnitude  $(M_L)$  value recorded was equal to 2.3. The earthquakes were located using the Hypoellipse algorithm (Lahr, 1989) and the 1D crustal velocity model. Therefore, the data recorded by the permanent seismic network were integrated with the P and S phases related to the stations of the *Fiumenet* network. This integration allowed to obtain a good hypocentral location of local micro-earthquakes recorded by a small number (2-3 maximum) of stations of the permanent seismic network and therefore not analytically localizable. A peculiar microseismicity, clearly visible only at the *Fiumenet* seismic stations, have been identified.

We calculated the fault plane solutions of the most powerful earthquakes. A cross-correlation analysis in order to evaluate the similarity of waveforms useful to identify earthquakes families was carried out.

This microseismic swarm also produced tilt variations on a Mt. Etna permanent clinometric station, located near the epicentral area.

All these early observations provides new valuable elements useful in order to better understand the microseismicity along this fault and its relative dynamic.

### New constrains for the mantle source of quaternary lavas from the Hyblean plateau as evidenced by a combined study of trace elements and Sr-Nd-He isotopes

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Keywords: Hyblean lava, mantle source, Noble gases, Fluid inclusions.

Tholeiitic basalts, basanites and nephelinites from the Hyblean Plateau were investigated for noble gases, trace elements and Sr-Nd isotopes.

The variable Sr-Nd isotopic composition of studied lavas (<sup>87</sup>Sr/<sup>86</sup>Sr ranging from 0.70275 to 0.70331 whereas <sup>143</sup>Nd/<sup>144</sup>Nd varying from 0.51293 to 0.51316) is interpreted as a consequence of: (1) cryptic metasomatism events or (2) patchy partial melting. In the first hypothesis, the presence of a metasomatising component with "enriched" Sr-Nd isotopes would alternate to a primary mantle source featured by a "depleted" Sr-Nd signature, conferring a geochemically heterogeneous aspect to the mantle; on the contrary in the second hypothesis, the fractionation of Rb from Sr and of Sm from Nd during partial melting would have led over time to depleted and enriched mantle horizons.

Contrary, the isotopic geochemistry of helium evidences an almost constant <sup>3</sup>He/<sup>4</sup>He ratios (about 7.0 Ra), characterizing the entire dataset of samples. The apparent contradiction between He-Sr-Nd isotopes can be reconciled by speculating the presence, in the lithosphere beneath the Hyblean Plateau, of periodic "flushing" by deep He-rich fluids. This flushing would be capable of mitigating the geochemical variability between depleted and enriched mantle portions, so as to attribute a homogeneous helium isotopic marker of ~7 Ra.

This isotopic helium marker is comparable to that of mantle xenoliths sampled in the same area, evidencing a geochemical parentage between the Pliocenic-Pleistocenic volcanic rocks and the xenoliths. Opposite results are evidenced by the trace element geochemistry where the higher La/Yb and Ce/Yb ratios and the lower Zr/Nb ratios of mantle rocks with respect to the lavas allowed to hypothesize the presence of metasomatic carbonatitic melts, probably related to slab relicts of an 'old' subduction in the shallower mantle portions from which the xenoliths would come (Sapienza et al., 2005). In this framework, the quaternary lavas would originate from deeper mantle horizons not interested by contaminating agents and during their rise toward the surface, would sample part of this overlying metasomatised lithosphere in the form of mantle xenoliths.

Sapienza, G., Hilton, D.R. & Scribano, V. (2005): Helium isotopes in peridotite mineral phases from Hyblean Plateau xenoliths (southeastern Sicily, Italy). Chem. Geol., 219, 115-129.

# Eruption triggers and their timescales at Vulcano (Aeolian Islands): evidence from textural and in situ compositional data on plagioclase crystals

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Keywords: timescales of magma storage, pre-eruptive dynamics.

An integrated study of the textural and in situ compositions of plagioclase crystals erupted at Vulcano (Aeolian Islands) throughout the last 1000 years has led to the definition of the multi-level structure of the volcano plumbing system either for what concerns its working modes or the timescales of magmatic processes. Two centers have been active in historical times on the island: 1) Vulcanello, which was characterized by emission of poorly evolved magmas; 2) La Fossa Cone, which generally erupted more differentiated products. Our data suggest that storage and processes of magma diversification occur into an articulated plumbing system that is developed from the mantle-crust boundary up to the surface. In this regard, our data indicate the presence of at least three main magma levels of magma storage, which were variously activated over the last 100 years of activity. The deepest reservoir fed the basaltic-shoshonitic activity at both Vulcanello and La Fossa Cone. Indications for the presence of the other levels of magma storage are only from volcanic rocks feeding the eruptions at La Fossa Cone. Plagioclase crystals registered the ascent and continuous episodes of magma recharge plus mixing that affected these shallower reservoirs. The first stages of activity at Vulcanello were fed by poorly differentiated melts that rapidly ascended from the deep basaltic-shoshonitic reservoir, and later resided for limited time into the crust before the eruption. Sr diffusion modeling indicates very short timescales of crystal residence (<2 years) for plagioclase found in Vulcanello products. Plagioclase crystals in volcanic rocks erupted at La Fossa Cone give timescales of residence on the order of 2-10 years. These timescales are conflicting with prolonged magma storage in the shallow part of the plumbing system. Conversely, magma feeding the activity at La Fossa Cone are in accordance with storage for most of the time in reservoirs located below ~11 km of depth (i.e., where plagioclase is not stable) and intruded later at shallower levels only few years before the eruption. Activity at Vulcano could be therefore explained through repeated episodes of recharge and mixing involving the multi-level structure of the plumbing system. These consequential occurrences have as triggering mechanism the ascent of deep basic magma from the mantle-crust boundary.

### Volcanological history and magmatic evolution of Ustica island (southern Italy) from a new geological mapping (scale 1:10 000)

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Keywords: volcanological history, Ustica, magma storage and ascent.

A new geological mapping of Ustica Island (southern Italy) at 1:10.000 scale is here presented as the result of geological and structural fieldwork and remote sensing analysis, combined with literature radiometric ages and a large set of original petrochemical data. The eruptive, structural and magmatic history of Ustica is described as a result of four major growth stages (Eruptive Epochs 1-4), interrupted by prolonged periods of quiescence and marine erosion and deposition. The oldest hyaloclastites and pillow lavas (Epoch 1, ~737 ka) are related to ENE-WSW oriented fissural submarine activity. The emergence of the island corresponds with the emission of the mildly subalkaline basalt and andesite lavas and pyroclastic products relative to Mt. Guardia dei Turchi and Mt. Costa del Fallo stratovolcanoes (Epoch 2, 519-476 ka), forming the main WNW-ESE elongated volcanic relief in the middle of the island. Along the western coast of Ustica are present the coeval minor eruptive centers of Spalmatore and Punta di Megna, together with the offshore pyroclastic vent of Casa Zacami. The subsequent activities of Mt. Costa del Fallo (Epoch 3, 424-412 ka) is characterized by the Grotta del Lapillo trachytic pyroclastic products and a laccolite body, passing to mugearitic lava flows. A prolonged period of quiescence is recorded in different marine terraces raised at elevations of ~100 m asl due to regional tectonic uplift. Renewed activity produced the sightly differentiated Na-alkaline pyroclastic products of the Capo Falconiera tuff cone, formed during the Last Interglacial (~120 ka) during a period of prevailing marine erosion and deposition. Preliminary geochemical and petrologic data suggest that the tectonic setting along the history of the island has greatly influenced the dynamics of magma storage and ascent. In this view, the wide spectrum of bulk rock compositions (from basalts to trachytes) would reflect the intensity of extension in the area.

### Vertical motion, structural features and stratigraphic architecture of the Neapolitan Yellow Tuff (NYT) collapse caldera-resurgent dome system off the Pozzuoli Bay during the last 10 ky

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Keywords: High-resolution seismic profiles, Pozzuoli Bay, Sea-floor deformation.

Seismic stratigraphic analysis of very high-resolution single channel reflection seismic profiles provided insights into the last ~10 ka vertical deformation pattern in the submerged part of the Campi Flegrei resurgent caldera, off the Pozzuoli Bay. The collapse of the central part of the Campi Flegrei is associated with the eruption of the Neapolitan Yellow Tuff (NYT) at ~15 ka BP, and was followed by discrete phases of intracaldera volcanic activity and resurgence (Di Vito et al., 1999). Only in recent years the southern part of the caldera, presently submerged off the Pozzuoli Bay, has been explored using marine geophysical data (Sacchi et al., 2014; Steinmann et al., 2016). Interpretation of the high-resolution seismic reflection dataset acquired during the Cruise SEISTEC 2013, calibrated by marine gravity cores, allowed us to identify key horizons between the 1538 AD M. Nuovo and the ~3.7 ka Averno eruptions. Chronostratigraphy of the older part of the caldera fill was inferred through tentative correlation with significant eruptions known onland. Seismic stratigraphic interpretation reveals the occurrence during the last  $\sim 10$  ka of at least three generations of Prograding Wedges (PW1-PW3) that were likely associated with corresponding periods of relative sea-level stands, and of minor coastal terraces. Correction of the observed depth of each sea-level indicator for the paleobathymetric estimate and for the glacio-hydro-isostatic sea-level change occurred since its formation, allowed to reconstruct differential relative sea-level curves for the western, central and eastern sector of the submerged part of the caldera. Preliminary results indicate that the periods of relative sea-level and accommodation space stability that allowed the onset of Prograding Wedges were attained when uplift occurred at a rate comparable to the rate of sea-level rise. These periods ostensibly correspond to known different phases of volcanic activity and unrest, suggesting that not only volcanism but also ground deformation were temporally clustered. Subsidence prevailed during periods of volcanic quiescence.

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#### Chemical and redox variation in Etnean magmas in the last 15 ka

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Keywords: silicate melt inclusions, experiments, oxygen fugacity.

In order to understand the chemical variations and volatile emissions and constrain redox conditions, petrological investigations and modeling of Mount Etna magmas have been performed.

Olivine-hosted melt inclusions (MIs), belonging to products of the last 15 ky, were analysed for their chemical composition, volatiles contents and Fe speciation. They were selected from the most primitive Fall Stratified (FS,  $Fo_{89.91}$ ) and Mt. Spagnolo ( $Fo_{82-88}$ ) eruptions and among the more recent 2002-2013 ( $Fo_{68-83}$ ) products. Crystal fractionation and degassing processes were modeled at temperatures of 1050-1300 °C, pressures <500 MPa, and oxygen fugacity ( $fO_2$ ) between 1 and 2 log units above the Nickel-Nickel Oxide (NNO) buffer. In addition, to better interpret sulphur contents in MIs, S solubility experiments were performed under variable  $fO_2$ .

MIs show a high variability in major elements chemistry (e.g., 3-15 wt.% CaO, 4-13 wt.% FeO, 2-12 wt.% MgO, 1-6 wt.% K<sub>2</sub>O). This outlines a continuous differentiation trend from FS toward 2013 compositions, satisfactorily modeled by fractional crystallization of olivine + spinel + clinopyroxene  $\pm$  plagioclase, in order of appearance.

Volatile contents are also extremely variable between MIs, with maxima up to 5.86 wt.%  $H_2O$  and 0.59 wt.%  $CO_2$  in FS, and up to 0.42 wt.% S in Mt. Spagnolo. The measured  $H_2O$  and  $CO_2$  contents suggest minimum entrapment depths of 12-18 km (below crater level) for FS MIs and < 10 km for the 2002-2013 trachybasalts.

Experimental results show the prevalent role of  $fO_2$  in controlling the sulphur content of Etnean hydrous melt and its partitioning between fluid and liquid phases ( $D_s^{\text{fluid/melt}}$ ): S solubility increases with the increasing of oxygen fugacity, while  $D_s^{\text{fluid/melt}}$  drastically decreases.

Fe<sup>3+</sup>/ $\Sigma$ Fe ratios have been obtained for some MIs from XANES measurements. They generally decrease from the most primitive and volatile-rich MIs (FS) to the most evolved and degassed melts (2013), suggesting that  $fO_2$  progressive decreases with differentiation. Modeling suggests that this Fe<sup>3+</sup>/ $\Sigma$ Fe decrease can be attributed mainly to melt differentiation. S and H<sub>2</sub>O degassing is also involved when conditions become less oxidized.

Petrological inferences, coupled to modelling of magmatic processes, suggest that most of the chemical variability in the Etnean magmas in the last 15 ka can be ascribed to differentiation mechanism, although a minor part of the variability requires heterogeneity in the mantle source. Magmas from Mt. Spagnolo and the recent eruptions can be produced essentially by differentiation from the most oxidized and hydrous pristine FS magma. The lowering in  $fO_2$  associated with the magmatic evolution induces a decrease of the sulphur solubility in the basaltic melt and promotes S partitioning toward the fluid phase. This mechanism probably triggers the important S degassing observed at Mt. Etna.

# Fast-diffusing volatiles record timescales of magma ascent and degassing leading to high-energy eruptions

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Keywords: Ascent rate, diffusion modeling, volatiles.

The rate at which magmas ascend and degas directly affect the explosivity of an eruption, thus the temporal quantification of such processes is a key element for the evaluation of hazard associated to violent explosive eruptions at active volcanoes. Diffusion chronometry in minerals and glasses of trace elements and volatile components characterized by very high diffusivities offers the chance to obtain direct measurements of such short-lived processes, which are too fast to be captured by diffusion of most major and trace elements. We are modeling the diffusion profiles of H2O, CO2 and S along olivine-hosted melt tubes and the diffusion Li zoning in plagioclase to track the degassing and ascent histories of volatile-saturated magmas during powerful explosive eruptions at open-conduit volcanoes (Giuffrida et al., 2018). We have selected as case study some exceptionally violent eruptions that were generated at New South East Crater and the Voragine crater of Mt. Etna between 2011 and 2016 Eruptions have been selected based on different intensities of the explosive activity, with the final aim to produce an array of ascent rates for a range of possible eruptions at open-conduit systems emitting low viscosity basic magmas. Diffusion modeling of volatile profiles across olivine melt tubes allows us to obtain timescales over which volatiles have been exchanged by diffusion with the adjacent melt as it evolves, and it offers insights into the magma degassing and ascent paths at shallow depth. The rapid depletion of Li from the melt during the gas phase separation upon eruption yields an outward decrease of the Li concentration in plagioclase. The resulting Li gradients are easily erased by diffusion unless the melt is rapidly quenched to glass during the eruption. Thus, measurements and diffusion modeling of Li concentration gradients in plagioclase lead us to recover timescales of the final stage of magma ascent and degassing, just before the emission at surface. Preliminary findings of our study indicate that re-activation of the magmatic system at open-conduit volcanoes erupting low viscosity basic magmas can occur over exceptionally short timescales, and it is likely triggered by gas flushing. Retrieved timescales are comparable to the timescales of syn-eruptive magma ascent derived for closed-system volcanoes on Earth, which emit evolved magmas through violent Plinian eruptions.

Giuffrida, M., Viccaro, M. & Ottolini, L. (2018): Ultrafast syn-eruptive degassing and ascent trigger high-energy basic eruptions. Scientific Reports, 8, 147.

# Exceptional discovery at Panarea island! The unique recent iron Ooids deposit known in the world: multidisciplinary study to constrain their hydrothermal/volcanic origin

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Keywords: iron-ooids, Panarea Island, hydrothermal fluids.

Exploration strategy aimed at discovering clues of submarine hydrothermal systems is strongly relied on the occurrence of surface evidences of subsurface geothermal energy. In the subduction-related volcanic arc setting of the Aeolian Islands, a primary role is played by the submarine hydrothermal activity that generated in different steps iron oxydroxydes and sulfur deposits over the whole archipelago. In the last years, the Fe-rich depositions representa research topic of interest in providing genetic implications on similar terrestrial as well as Martian deposits.

In this scenario, during a cruise carried out by ISPRA and INGV on board of the research vessel Astrea, a sand deposit was sampled off the Panarea Island. The sample turned out to be an exceptional discovery, because it represents the unique, recently formed, not diagenetic and not reworked iron ooids deposit, known to date in the world. Iron ooids are an important component of the sedimentary record since Precambrian times; their formation, however, is not yet fully understood. Results of the preliminary studies of the Panarea ooids - able to constrain their hydrothermal origin and to provide a first genetic model- are here reported. The deposit occurs over an area marked by diffuse submarine hydrothermal discharge consisting of diffuse venting of thermal waters andgas bubbles streams.

An integrated textural, mineralogical and geochemical characterization of iron ooids was performed. The results showa good matching with those from ancient sedimentary counterparts. Panarea ooids are made by concentric goethite laminae deposited around nuclei of particles present on the seafloor. The process was abiotic, rapid and ruled by  $CO_2$ -rich hydrothermal fluids. Compared with the other components of the hydrothermal system, the iron coating shows some HREE enrichment. In this regard, a genetic model in which  $CO_2$  rich hydrothermal fluids interact with the hosting rocks in a rhyolitic reservoir and mobilizing incompatible trace elements, including REE and others, is here proposed. As a matter of fact, the hydrothermal fluids become carriers of iron, silica, REE and LILE, as well as of low amount of Nb and Zr. As soon they rise up through the sea-floor sediments and interact with the colder sea water, in an oxidizing sediment/seawater interface, the oxyhydroxides flocculate.

The overall results constrain the hydrothermal/volcanic origin of the coated grains, define them as the precursor grains of older iron oolite sand may also contribute to interpret analogue particles recently discovered on Mars. This contribution combines monitoring data and a multidisciplinary approach for understanding environmental events that frequently occurred during the Earth evolution.

#### Mt. Etna: geochemical evidences to understanding how the volcanic system works

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Keywords: Mt. Etna, geochemical evidences, volcanic system.

Mount Etna is an open-conduit basaltic stratovolcano located near to the collision boundary between African and European plates. Its peculiar geodynamic setting and its persistent activity make the volcano an extraordinary site where scientists can observe a wide range of eruptive dynamics (ash emissions, Strombolian activity, fire fountains, and effusive eruptions) and collect many kinds of evidences to better understanding how the volcanic system works. Volcanogenic elements are emitted to the earth surface as both solid and gaseous products and can bring useful information on the processes occurring within the volcanic system. In recent years, many geochemical investigations were carried out, thus providing new insights on the chemical and isotopic composition of volcanics, gases and groundwaters. Results allowed describing geochemical features in the mantle source, dynamics and redox conditions in the magmatic system and physico-chemical processes in the hydrothermal reservoirs, by using tracers as noble gases and sulfur (Liotta et al., 2010, 2012; Paonita et al., 2012, 2016a; Rizzo et al., 2013). The studies also showed that the quiescent degassing and the rising of deep fluids affect the circulating groundwater (Liotta et al., 2016, 2017; Paonita et al. 2016b).

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# Tracing groundwater flow-lines and the interaction with degassing sources analysing dissolved inert gases (He, Ne, N<sub>2</sub>) in Etnean aquifers

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Keywords: Dissolved gases, helium isotopes, volcanic groundwater.

In volcano edifices hosting aquifers, a large amount of magmatic gases rising from deep is trapped and carried by groundwater. Several studies in the past three decades have demonstrated the role played by monitoring chemical and isotopic composition of dissolved gases in groundwaters hosted in volcanic area, which represents by now a powerful tool to evaluate the state of activity of volcanoes and its evolution. The first step to make it possible, is a comprehensive understanding of fluids circulation inside the volcano edifice, starting from groundwaters characterization up to the identification of the underground pathways and their relationships with tectonic structures, that enhance interactions between waters and magmatic gases. In this work, we focussed on chemical composition of inert dissolved gases (He, Ne, N<sub>2</sub>) and He isotope abundances coming from groundwaters circulating in Mt. Etna, as having great contrast between magmatic and shallow sources and no chemical interaction with rocks. We identified waters which intersect anomalous degassing areas, such as well evident or buried tectonic structures. These waters show both nearly magmatic He isotopic composition and high ratios of dissolved magmatic gases (He, CO<sub>2</sub>) versus the atmospherics ones (N<sub>2</sub>). Along the hydrologic flow-lines and faraway from the degassing structures, we found waters with lower He isotopic ratios and consequently richer of atmospheric-derived gases (Ne, N<sub>2</sub>). On this basis, we set-up a model of unidimensional dispersion-advection, coupled to a two-layer dynamic exchange of volatiles between the aquifer surface and atmosphere. (Paonita et al., 2016). The model is able to quantitatively explain the progressive "dilution" of the magmatic signal through several kilometres-long distances, from the source point of the anomaly towards the final stage of flow-lines at the coast. Typical hydro geological parameters, such as rock permeability, could be constrained by this approach. Moreover, anomalous compositions found along water flow-lines could represent possible new sources of degassing, allowing to detect hidden degassing structures.

Paonita, A., Longo, M., Bellomo, S., D'Alessandro, W. & Brusca, L. (2016): Dissolved inert gases (He, Ne and N<sub>2</sub>) as markers of groundwater flow and degassing areas at Mt. Etna volcano (Italy). Chem. Geol., 443, 10-21.

### Eruptibility of magma at calderas

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Keywords: sill intrusion, caldera.

We investigate the conditions for the eruptibility of magma intruded at shallow depth in calderas. We assume that during magma intrusion a major role is played by melt viscosity, crystal fraction and gas content. We adopt the alphaMelts code for the simulation of the thermodynamic evolution of the melt and we consider the spatial distribution of the stress induced in the host-rock by a sill intrusion as factor that can promote an eruption. We simulate the intrusion of the sill in two different types of calderas: mafic and felsic. Finally, we compare our results with the outcomes of a statistical analysis on a dataset of unrest at calderas. In particular, we compare the simulated evolution of the unrest in terms of eruptibility and induced stress with the distribution of the duration at real eruptive or non-eruptive unrest episodes at calderas. Results show the importance of magma viscosity and the stresses induced on the host-rock by the sill to determine its eruptibility.

### The sub-surfacestructure of the south-eastern Valledel Bove (Mt Etna, Sicily) as imaged by high-resolution seismic reflection data

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Keywords: high resolution seismic reflection, M.te Etna, Valle del Bove.

Valle del Bove (VdB) is a wide horseshoe-shaped depression, produced since 9 ka ago by gravitational collapses of the eastern flank of Etna volcano, dismantling old volcanic centers (Branca et al., 2011) and leading to the formation of the Milo Lahar debris avalanche and the Chiancone detritic-alluvial coastal deposit (Calvari et al., 2004).

In summer 2017 the INGV and the CGT undertook a project, granted by ACOSET S.p.A.,to better constrain the relation between flank instability and tectonics in the outlet of VdB, near the villages of Milo and Zafferana Etnea. Using a high-frequency vibratory source (VibroSeis), three N-S oriented high-resolution seismic reflection profiles for a total length of about 5.5 km were acquired. In particular, the main target wasto investigate the shallow portion (about 500 m deep) of VdB outlet, in order to:(a) study the seismo-stratigraphicsequence of thissector of the volcanic edifice; (b) characterize the volcano-clastic deposits related to the VdB collapse; (c) evaluate the depth and the morphology of the sedimentary substratum below the volcanic pile; (d) identify subsurface trend and geometry of the main tectonic structures.

Volcanic areas represent a very complex environment for seismic exploration, mainly due to the strong heterogeneities of volcanic products andtheir uneven morphology. Data were collected using a Dense-WideAperture(DWA) array (Bruno et al, 2013) made of 240 vertical geophones, 5 m spaced, with a 4.5 Hzeigen-frequency.

This geometry allowed a meaningful interaction between refraction and reflection data processing (useful as support in the definition of velocity field) and overcome most of the factors that limit the data quality in those environments. Given also the uncertainties in the definition of a reliable velocity field in these environments, to improve data quality, we used the Common Reflection Surface stack, that is velocity-independent method to produce stack with high signal-to-noise ratios enhancing images of dipping reflectors (see Mann et al., 1999 and reference therein).

Volcanic activity products of the recent Mongibello volcano (< 15 ka, Branca et al., 2011) return mid-amplitude signals, resulting in sub-horizontal, laterally continuous horizons in the 2D stacked sections. They locally are superor laterally imposed to an up to 150 ms (about 150 m) thick transparent seismic facies, likely corresponding to the Milo Lahar, which inthe eastern portion of the study area crops out with a maximum thickness of 30 m. These seismic facies overlie a high amplitude package of seismic horizons, below ca 200 ms, laterally interrupted through subvertical blanking zones. It represents a tectonically deformed substratum, related to the pre-Mongibello volcanics or to a sedimentary basement. Preliminary results outline the presence of a thick volcano-clastic deposit filling a tectonically controlled depression, improving the knowledge of the VdB formation.

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### Plumbing system geometry feeding the monogenic volcanic fields: inferences from basalts of the Northern Main Ethiopian Rift

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Keywords: Magma plumbing system, Ethiopia, monogenic volcanic fields.

Monogenic volcanic fields are made up of tens-to-thousands small monogenic eruptive centers. One of the main unsoved issues for global volcanology is how such a large number of monogenic eruptive centers form and what is their time of emplacement. Monogenic scoria cones are typical of complex settings like the Trans-Mexican Volcanic Belt and the Central Kamtchatka Depression, for what regards the comprenssional margins, or of some extensional settings such as the Northern Main Ethiopian Rift (NMER). All the extension in the NMER is accommodated by an oblique en-echèelon system of active faults at the floor of the Rift Valley (the Wonji Faults Belt), which is also the main site of volcanic activity. Here, volcanism is characterized by central volcanoes (Fantale, Kone, Boseti, Gedemsa), eruptive fissures with lengths of several kilometers and small basaltic monogenic scoria cones (MSC are >200 in the NMER) with associated minor lava flows, aligned along the Wonji segments. Although it is not possible to derive the exact temporal evolution of volcanism in the area, the petrographic and geochemical bulk features of volcanic products show important differences. Fissural products have trachybasaltic composition and are aphyric (Porphyritic Index P.I. <1-2 vol.%), whereas MSC are basalts with P.I. 15-30 vol.%, with plagioclase phenocrysts as the dominant phase (up to 90% among the phenocrysts). Mass balance calculations showed a same parental magma for all these products, but different crystallization histories. MSC products derive from the shallow fractionation of about 15 vol.% of crystals (consituted by Ol, Cpx, Ox, Opx) in addition to plagioclase cumulates on the order of of 30-40 vol.%. Magmas erupted thorugh fissural systems underwent more extensive fractionation (35 vol.%) of the same mafic phases. The integration of geological observations along with petrographic and geochemical data allow us to put forward the idea that: 1) fissural trachybasaltic magmas resided at the Moho, where they fractionated mafic phases: when eruption was triggered (probably for tectonic reasons), they rose up directly to the surface through fault systems; 2) MSC basaltic products derive from low-pressure crystal fractionation (<10-12 km) of a magma which rose up from the Moho through the lithospheric Wonji faults and was stored at crustal levels (above the plagioclase nucleation depth, estimated at about 11 km of depth) with a shape elongated along the main fault system; here, basaltic magmas started to crystallize. In agreement with this picture, monogenic volcanic fields appear to be the result of slow ascent of several small-volume blobs of magma (mainly depending from density contrasts) from rather shallow magma reservoirs.

#### Episodic slow slip events and seaward flank motion at Mt. Etna volcano (Italy)

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Keywords: flank instability, Mt. Etna, GPS and InSAR measurements.

Evidences of flank instability has been documented at Mt. Etna volcano since the early 1980s. In particular, GPS and InSAR measurements as well as geostructural data have concurred in identifying a near continuous seaward motion of a large sector of Mt. Etna eastern flank (e.g. Palano, 2016). Such an unstable sector is delimited by the "NE Rift -Pernicana fault" and by the "S Rift - Mascalucia-Tremestieri fault", respectively on its NW and SW half, while the presence of compressional structures (e.g. folds) has recently been observed at the toe of the continental margin, on the Etnean offshore (Gross et al., 2015). In addition, a prominent ESE lineament with prevailing right-lateral transpressive kinematics, located northward of Catania Canyon and considered as the off-shore prolongation of the Mascalucia-Tremestieri fault, has recently been discovered (Gross et al., 2015). The definition of the basal sliding surface is widely debated and a number of different models have been proposed in the last 3 decades: i) a shallow (~1.5 km) slip surface with a listric geometry located beneath the volcanic pile of Mt. Etna; ii) an approximately 5-km-deep sub-horizontal décollement occurring in quaternary sedimentary units; iii) alternating or contemporaneous movements on both shallow and deep slip surfaces; iv) a décollement surface located at a depth ranging from 1 to 4 km bsl.

The establishment of a CGPS network has allowed detecting, since mid-2008, some aseismic slow slip events (SSE) from the daily-based time series of stations installed on the lower part of the unstable flank. At Mt. Etna, SSEs have probably been going on for a long time, but they have not been recognized because the campaign measurements carried out yearly since 2001 provide a broad snapshot that showed a fairly constant rate of motion of the flank. Here, taking advantage of the availability of CGPS data, we provide a catalog of SSEs times as well as the spatial distribution of modelled slip on a décollement surface.

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# Magma transport and storage at Mt. Etna volcano (Italy): an improved perspective from two decades of geodetic and petrological observations

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Keywords: plumbing system, petrological observation, Mt. Etna.

Mt. Etna volcanic activity has been characterized, in the last two decades, by more than 100 paroxysmal events (from moderate to intense and impulsive explosive activity, coupled sometime to voluminous lava flows) as well as by some large eruptive events (e.g., 2001, 2002-03, 2004-05, 2006, 2008) involving the upper sector of the northern and southern flanks of the volcano, along with the summit craters. Taking advantage of the availability of an extensive dataset of continuous GPS stations installed on the upper sector of the volcano edifice, we proposed an unprecedented and detailed picture of different deformative stages occurring at Mt. Etna. The surface deformation for each detected stage was used to constrain isotropic half-space elastic inversion models, therefore providing significant constraints on subsurface Mt. Etna's magma storages and conduits. In addition, a number of petrological observations on volcanic rocks (lavas and tephra), which were collected on the field during the on-going eruptive activity, provided relevant constraints on the timescales of magma storage and transfer at various levels of the volcano plumbing system. Finally, the joint interpretation of constraints coming from geodetic data and petrological observations allowed us to provide an improved model of magma ascent history as well as the complex interactions that affected various magma batches during the investigated period.

### Active geodynamic in the central Mediterranean: Transfer of mantle fluids across the eastern Sicily

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Keywords: helium isotops, magmatic intrusion, tectonics.

Mantle degassing occurs principally through active volcanic systems and young oceanic lithosphere. Tectonically active regions on the continental crust may additionally contribute a (poorly quantified) fraction of the deep  $CO_2$  budget. He is a powerful tracer to recognize the release of mantle volatiles, which are enriched in <sup>3</sup>He relative to the crust.

We studied volatiles in thermal manifestations along the seismically active Nebrodi-Peloritani chains (NE Sicily), to investigate the origin of thermalism and fluids. The geological evolution of the area has been controlled by the interaction between the European and African plates and links the African Maghreb with the European Apennines.

The collected samples exhibit <sup>3</sup>He excess, supporting active outgassing of mantle-derived volatiles. The computed mantle-derived He fluxes are up to 3 orders of magnitude higher than in stable continental areas. These high fluxes support advective fluid transport through regional tectonic discontinuities.

The area, despite being a chain, is located between two of most active volcanic systems, Mt. Etna to south and the Aeolian arc to north. Geophysical studies and experimental models (Piromallo et al., 2003) suggest the existence of toroidal flows in the mantle that, bypassing the subduction plate, produce mantle upraise in the area (Faccenna et al., 2011), eventually leading to magma accumulation at the mantle-crust interface, or in the crust. We propose gas ascent occurs via the Eolie-Tindari-Letojanni fault system (ATLFS), interpreted by either an offshoot of a regional lithospheric structure in the Ionian Sea (Polonia et al., 2016), or a slab tear or STEP type structure at the margin of subduction ionian plate (Doglioni et al., 2001). Our study supports a) the possible presence of magmatic intrusions below this sector of the Maghrebian-Apenninic chain, and b) the active role of the regional discontinuities in transferring mantle fluids towards the surface.

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### Natural clocks in volcanic rocks! Untangling magmatic processes fixing their tempo: what we have learned from the 2011-16 activity at Etna

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Keywords: Etna; eruptions, volcanic processes, diffusion modeling.

The increasing application of avant-garde in situ analytical techniques on crystals in volcanic rocks has led to an exponential growth on the comprehension of how volcano plumbing systems work. The exceptional awareness of the inner structure of volcanoes and of magma transfer and degassing processes driving the eruption onset requires, however, kinetic constraints to push forward frontiers of the modern volcanology. Among the multiple techniques of investigation of the plumbing system dynamics, analyses of textures and chemical zoning in minerals have been recognized as the most efficient tools. Results presented here synthetize important findings obtained through the combination of textural, chemical and temporal records of magmatic crystals from products erupted at Etna during the 2011-16 period. In this regard, eruptions of 2011-16 revealed to be an exceptional case-study, given the wide spectrum of explosive activity observed at the summit craters (i.e., New South East Crater during 2011-13 and Voragine during 2015-16), which encompasses from violent Strombolian ejections up to incredibly energetic lava fountaining. A huge compositional dataset of olivine crystals has been used to produce a realistic spatial-temporal reconstruction of magma dynamics preceding and accompanying the eruptive activity at the volcano. Chemical zoning in olivines highlights processes of multi-step magma transfer and residence into various magmatic environments, which have been characterized on the basis of the forsterite contents at the crystal cores and then constrained in terms of specific P-T-H<sub>2</sub>O-CO<sub>2</sub>-fO<sub>2</sub> through thermodynamic modeling. Results show that at least six main magmatic environments have been activated in distinct times throughout the 2011-16. Involvement of reservoirs placed at shallow or deep levels of the plumbing system well relate with critical moments of the eruptive events at the volcano, either for what concerns the style or the frequency of activity. Diffusion modeling in olivines also defines timescales of magma transfer and storage throughout the identified magmatic environments, which are generally kept below the scale of 18 months. Results put also emphasis on the fact that more basic magma coming from the deepest environments of crystallization can be intruded and mixed into the shallowest reservoirs with exceptionally fast timescales, even on the order of only 1-6 weeks before the eruption. Thermodynamic constraints coupled with temporal quantifications of volcanic processes are therefore relevant for a full comprehension of dynamics leading to extra-ordinary, energetic eruptions at open-conduit volcanoes such as Etna, which is usually acknowledged for its effusive or weak-to-mild explosive activity. Importance of such studies in volcanology relies on the fact that convincing responses for what regards hazards at active volcanoes can be better achieved through the quantification of the parameter tempo of volcanic processes.

### Violent paroxysmal activity triggers rejuvenation of a volcano plumbing system: clues from the 2017 eruptions at Etna

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#### Keywords: Mt. Etna, 2017 activity.

During the first half of 2017, the volcanic activity of Etna resumed after almost 8 months of quiescence, with a new sequence of eruptions with low-to-mild intensity. A weak Strombolian activity started on January 2017 at a vent located between the old and the new cone of the South East Crater. The explosive activity became more vigorous during the night between February 27-28 and was accompanied by lava overflowing. Increase of the Strombolian activity occurred on March 15-17 with conspicuous ash emission from the same vent. Since March 16, a new vent opened on the southern flank of the South East Crater started to feed effusive activity, producing new lava flow fields just south of the summit area. Other minor episodes of explosive and effusive activity occurred until April 27, 2017. The weak volcanic events of 2017 might be viewed as a benchmark in the post-2011 eruptive activity of Etna, which was mainly characterized by violent paroxysms, as those of 2011-2013 at New South East Crater and of 2015-2016 at the Voragine Crater. All the erupted rocks are K-trachybasalts, with compositions similar to those of other recently erupted products. Geochemical analyses reveal, however, some differences in whole rock compositions of the 2017 volcanic rocks if compared to those of the other post-2011 products. Major differences have been observed with respect to products of the 2011-13 paroxysmal sequence, especially concerning some major and trace elements. Within this picture, the 2017 products show close affinities with those emitted at Voragine during December 2015 and May 2016, as suggested by variations of some incompatible trace element ratios. These data support the idea that the 2017 magmas can be the result of an evolution path different with respect to that followed by magmas erupted before the 2015-2016 eruptions at Voragine. Magma evolution could have been driven by progressive substitution of the residing magmas through recharge by new magma. Modeling of geodetic data also suggests that a first recharging phase by fresh magma occurred at depth of ~6.3 km bsl between June 2016 and early March 2017. In late March 2017, a volcano-scale deflation has been related to depressurization of a source located at depth of ~4.6 km bsl. All these observations suggest that the deep recharging magma progressively replaced the residual one as a consequence of a self-feeding rejuvenation mechanism of the volcano plumbing system, which is triggered by the violent paroxysmal episodes occurred at the Voragine Crater on May 2016.

# Session S22 Volcano Hazard Monitoring

Conveners And Chairpersons Ciro Del Negro (INGV, Catania) Fabrizio Ferrucci (Università della Calabria) Alexis Hérault (Conservatoire National des Arts et Métiers)

### Sensitivity of the MAGFLOW cellular automaton for lava flow simulations

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Keywords: sensitivity analysis, hazard assessment, lava flow simulation.

MAGFLOW is a physics-based numerical model for lava flow simulations based on the Cellular Automaton approach that has been successfully used to predict the lava flow paths during the recent eruptions on Mt Etna. We carried out an extensive sensitivity analysis of the physical and rheological parameters that control the evolution function of the automaton and which are measured during eruptive events, in an effort to verify the reliability of the model and improve its applicability to scenario forecasting. The results obtained, which include Sobol' sensitivity indices computed using polynomial chaos expansion, confirm the consistency of MAGFLOW with the underlying physical model and identify water content and solidus temperature as critical parameters for the automaton. Additional tests also indicate that flux rates can have a strong influence on the emplacement of lava flows, and that to obtain more accurate simulations it is better to have continuous monitoring of the effusion rates, even if with moderate errors, rather than sparse accurate measurements. Similar results are obtained for the topographic data, for which we show that level of detail of the digital elevation model (DEM) is less important than the recency of the data: on a volcano as active as Mt Etna, it is therefore important to update DEMs after every eruption, even with methods that provide information at lower horizontal resolution. Strategies to improve the reliability of the scenarios provided by MAGFLOW are also presented, building on the results of the sensitivity analysis.

### Dike intrusion energy balance from deformation modeling and seismic release: an approach to forecast the eruptive fissure propagation

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Keywords: dike propagation, dike deformation and seismic release, eruptive fissure hazard.

Magma is transported in the crust mainly by dike intrusions. In volcanic areas, dikes can ascend towards the free surface and also move by lateral propagation, eventually feeding flank eruptions. Understanding dike mechanics is a key to forecasting the propagation and associated hazard. In particular, longer is the expected fissure length then higher is the lava invasion hazard.

Several studies have been conducted on dike mechanisms and propagation; however, a less in-depth investigated aspect is the relation between measured dike-induced deformation and the seismicity released during its propagation. We individuated a simple equation that can be used as a proxy of the expected mechanical energy released by a propagating dike and is related to its average thickness. For several intrusions around the world (Afar, Japan, Mt. Etna), we correlate such mechanical energy to the seismic moment released by the induced earthquakes. We obtain an empirical law that quantifies the expected seismic energy released before arrest. The proposed approach may be helpful to predict the total seismic moment that will be released by an intrusion and thus to control the energy status during its propagation and the time of dike arrest. The comparison of the seismic moment expected by the release of the available energy with the moment calculated in real time by observing networks provides a potential prediction in the early phase of an eruptive intrusion of when the energy is balancing and hence when the dike is expected to stop.

#### Lava flows, lava tubes and lava fountains at Etna volcano: hazard assessment

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Keywords: lava flows, lava tubes, lava fountains.

The maximum lengths of aa lava flows are related to effusion rate (Walker, 1973). Thus, the maximum distance that a lava flow can attain can be estimated at the start of an eruption using a simple formula (Calvari & Pinkerton, 1998) that relates the maximum lava flow length to the peak instantaneous effusion rate (Harris et al., 2007). This is generally measured during the initial phases of an eruption (Wadge, 1981). However, there is evidence that the formation of lava tubes can significantly increase the final length of a long-lived aa flow field (Calvari & Pinkerton, 1998; 1999). In these cases, before using more complex lava flow models that are not able to simulate the effects of lava tubes, the maximum distance of the lava flow field could be estimated applying the same formula to any new first-order ephemeral vent opening at the front of arterial lava flows (Calvari & Pinkerton, 1998).

A more complex situation arises in cases of paroxysmal explosive activity, with lava fountains normally giving rise to powerful eruptive columns and ash plumes (Bonaccorso & Calvari, 2013; Bonaccorso et al., 2014). The volumes of pyroclastics erupted during lava fountain episodes can be obtained from the analysis of thermal images recorded from fixed monitoring cameras (Calvari et al., 2011; Bonaccorso & Calvari, 2017), and the extension of the ash plume can be estimated by using existing models of plumes' expansion.

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### Assessing lava flow hazards at the new Southeast Crater of Etna volcano

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Keywords: Pléiades imagery, Digital Elevation Model, MAGFLOW simulations.

The summit area of Mount Etna has undergone frequent morphological variations since the formation of the Southeast Crater (SEC) in 1971 and the New Southeast Crater (NSEC) in 2011, which have marked a real change in the eruptive activity of the volcano. Indeed in less than 50 years, SEC has been the source of more than two hundreds of eruptions characterized by the emission of lava fountains, pyroclastic material, and short-lasting lava flows, which are the greatest hazard presented to the tourist facilities on the south flank of Etna. For this reason, in 2011 we produced a lava flow hazard map for SEC eruptions using the 2005 DEM as topographic base, where the NSEC was not yet formed. Here we present the hazard map from lava flow inundation in the NSEC area on a new DEM produced by using satellite images from the Pléiades constellation acquired on 18 July 2016. The 3D processing of the tri-stereo Pléiades imagery was performed using the free and open source MicMac photogrammetric library (http://micmac.ensg.eu) and took advantage of field Ground Control Points (GCPs) placed on Mt Etna. The best result obtained with the Pléiades images of 18 July 2016 is a 1-m DEM spanning an area of 250 km<sup>2</sup> ( $\sim$ 16 km x 16 km), which covers the summit craters and a portion of the south-east flank of the volcano, including Valle del Bove. This DEM was used as the new topographic base to produce the first hazard map from lava flow inundation in the NSEC following the probabilistic modeling of Del Negro et al. (2013), which includes the development of the spatiotemporal probability map of future vent opening, the occurrence probabilities associated with the classes of expected eruptions, and numerical simulation of a number of eruptive scenarios by the MAGFLOW model. The resulting hazard map from lava flow inundation in the NSEC area allows key at-risk zones to be rapidly and appropriately identified.

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This work has been developed within the framework of TecnoLab, the Laboratory for Technological Advance in Volcano Geophysics of the INGV in Catania (Italy) and was partially supported from the DPC-INGV 2012-2021 Agreement. Pléiades data were available through the Space Volcano Observatory.

### Thermal signals in volcano monitoring: cross-checking MODIS-MIROVA data with ground-based measurements at Aso Volcano, Japan

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Keywords: Thermal signals, MODIS-MIROVA, unrest episodes.

Aso Volcano, also known as Nakadake, is the active cone within the Aso caldera in north-central Kyushu. This volcano lies on the Beppu-Shimabara graben trending ENE. Nakadake, is the only active volcano and eruptive products are predominantly andesitic and basaltic. The typical eruptive activity involves the summit lake, and the active fumarole field. An increase in the heat flux will induce the progressive evaporation of lake waters and phreatic/phreatomagmatic explosions may occur eventually leading to Strombolian eruptions. The last Strombolian phase started during the summer-fall 2014 and persisted until May 2015. In the following months, waters accumulated within crater and the lake progressively grew up again. During this span of time fumaroles were particularly active and the phreatic-phreatomagmatic activity was resumed, culminating with the major phreatic explosion of October 8, 2016.

The thermal signals of Aso Volcano (Nakadake) during unrest episodes have been analyzed by means of the MODIS-MIROVA data set (2000-2017) and high resolution images (LANDSAT 8 OLI and Sentinel 2) combined with ground-based thermal observations (2013-2017). The Volcanic Radiative Power (VRP) detected by nighttime satellite data during the time span considered was mainly below 3 MW. This value is a thermal threshold that marks the transition from high fumarole activity (HFA) to Strombolian eruptions (SE). Periods with the occurrence of sporadic phreatic eruptions (PE, eventually bearing phreatomagmatic episodes), is the dominant phase during unrest episodes, with VRP values around 0.5 MW. Conversely, during marked Strombolian phases (November-December 2014) the radiative power was higher than 4 MW, reaching peak values up to 15.6 MW (on December 7, 2014, i.e., 10 days after the major Strombolian explosion of November 27). Ground-based measurements, recorded by FLIR T440 Thermo-camera on the fumarole field of the South Area, shows that the heat-flux has been relatively stable around 2 MW until February 2015. The apparent temperatures measured on the fumarole field were around 490-575°C before the major Strombolian explosive event, whereas those recorded at the active vent, named Central Pit, reached their maxima slightly above 600 °C. In the following days they both exhibited a decreasing trend. However, during the Strombolian phase the crater lake dried out and was then replenished by early July, 2016. Then volcanic activity shifted back to phreatic-phreatomagmatic and the eruptive cycle was completed; in this period ground measurements were fluctuating around 1 MW. Following the major phreatic explosion of October 8, 2016 the VRP were moderately above 2 MW.

The cross-checking between satellite data and ground-based measurements proves that the firsts are sufficiently efficient in monitoring crater lake activity. These may be very useful during critical unrest episodes because they can minimize the exposure of researchers and technicians during field work.

### Artificial neural network approach to removing cloud cover from satellite imagery of volcanoes

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Keywords: remote sensing, hot-spot detection, SEVIRI.

Thermal Infrared (TIR) remote sensing measurements of high-temperature volcanic features improve our understanding of volcanic phenomena and our ability to identify renewed volcanic activity. However, one of the major problems of remote sensing techniques for thermalmonitoring of volcanic activity is the detection of cloud-contaminated pixels. Indeed, in the case of thermal volcanic activity, cloud coverage could generate false alarmssuch as missing identifications. Here, we present a method based on artificial neural networks (ANNs) for cloud detection through satellite image analysis. Neural networks are an effective and well-established technique for the classification of satellite images. In addition, once well trained, they prove to be very fast in the application stage. The proposed method is a supervised classifier that exploits radiance spatial correlation in satellite images using a statistical descriptor of texture rough neural networks. Cloudy and clear-sky models are determined using cluster analysis over the image features. The pixels to be classified are compared with the estimated models and assigned to the closest model. The cloud detection algorithm has been tested on a data set of MSG-SEVIRI images acquired in the area of Etna volcano. Results show that the proposed method can be considered effective both in terms of classification accuracy and generalization capability. In particular our approach proved to be robust in the rejection of false positives, often corresponding to noisy or cloudy pixels, whose presence in multispectral images can often undermine the performance of traditional classification algorithms.

## Far field thermal boundary condition in lava flowing in an open channel

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Keywords: Numerical modeling, viscous dissipation, boundary conditions.

Cooling and dynamics of lava flowing in a rectangular channel driven by the gravity force is numerically modeled. The purpose is to evaluate the heating of the solid boundary that flank lava as a function of time. Lava rheology is dependent on temperature and on strain rate by a power law function. The model couples dynamics and thermodynamics inside the channel where lava flows and describe the thermal evolution of the solid boundary which enclose lava channel. Numerical tests indicate that the solution of the thermo-dynamical problem is independent of the mesh. The boundary condition at the ground and at the levees is treated assuming a solid boundary around the lava flow with which lava can exchange heat by conduction. Far field thermal boundary condition allows to overcome the assumption of constant temperature or constant heat flow as boundary conditions, providing more realistic results. The effect of viscous heating is evaluated and discussed.

# Estimation of uncertainty in lava effusion rate integrating thermal infrared and tri-stereo optical satellite data

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Keywords: Volcanic hazard, satellite remote sensing, uncertainties.

During basaltic eruptions, the average rate at which lava is erupted (effusion rate) is one of the most important factor controlling the evolution, growth and extent of the flow field. This has implication both for forecasting purposes as input parameter into physics-based numerical models, and for advancing knowledge on the shallow feeder system by constraining the mass supplied.

Satellite remote sensing provides a means to estimate the average effusion rate over a specified period (Time Averaged Discharge Rate -TADR) by applying a direct conversion from the measured radiant heat loss by an active lava flow. This conversion relies on a set of parameters of lava (e.g. rock density, heat capacity, vesicularity, emissivity, etc.) and suffers of multiple sources of uncertainties and measurements errors, whose quantification is still an open problem.

Here we attempt to constrain SEVIRI-derived TADRs for two short eruptive events occurred on Mt Etna on 6-8 December 2015 and 17-23 May 2016, by using pre-eruptive and post eruptive digital elevation models (DEMs) obtained processing satellite images acquired by the Pléiades constellation, which provide images at 50 cm resolution in stereo and tri-stereo mode. The 3D processing of the tri-stereo Pléiades imagery (acquired on 28 July 2015, 18 December 2015 and 18 July 2016), performed using the free and open source MicMac (Multi-images Correspondances, Méthodes Automatiques de Corrélation) photogrammetric library provided estimations of the bulk volume emitted and of the distribution of thickness. Preliminary integration of SEVIRI-and Pléiades-derived results allow us to reduce the range of uncertainties for TADR estimation and represents a new potential of merging capabilities to enable a more comprehensive response to effusive crises.

# A model for the simulation of lava flows

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Keywords: volcanic hazard, lava flows.

We present a depth-averaged lava flow model valid in the approximation of purely viscous flow at low Reynolds number. Magma is modelled as a viscous fluid of costant density subject to gravity, flowing over an irregular surface. We assume temperature-dependent viscosity and we account for cooling by radiation, convection and conduction. The model reproduces analytical solutions and laboratory experiments. Moreover, the model was applied to real cases such as Etna eruptions showing good agreement between observations and simulations. The algorithm is implemented on a PC and can be easily incorporated into GiS for estimating the hazard from lava invasion during an eruption. Typical computer time range from few seconds to several minutes.

#### Spaceborne support to the prediction of lava distances to run: a discussion

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Keywords: remote sensing, thermal volcanic features, radiant fluxes.

The prediction of distance to run is a key-activity in support to risk mapping and or planning of emergency responses to eruptive (effusive) volcano events. Distance-to-run is driven by several chemical and physical parameters, and can be approached by estimate of mass eruption rates through their radiant flux proxy.

Radiant fluxes mainly depend on spectral emissivity, which is defined as the efficiency of physical bodies in radiating thermal energy at a specific wavelength: it is seldom measured and mostly assumed to be  $\varepsilon = 1$  or 20% less ( $\varepsilon = 0.8$ ), and not to change as a function of temperature and wavelength. However, true emissivity has substantial importance in passive remote sensing, due to its close relationship with the wavelength depending Land Surface Temperature, and the inherent impact on the estimate of mass eruption rates.

To fill this gap in knowledge involving spectral emissivity, we set up a programme of systematic in-lab measurement of spectral emissivity on rock samples by three independent methods, by FTIR spectroscopy between 0.4÷14.5 µm wavelengths and at temperatures between 400K÷1000K. Rock samples were collected on Mt. Etna in sampling grids scaled to the spatial resolution of High-Resolution multispectral payloads provided with Thermal Infra-Red channels on-board Landsat-5, Landsat-7 and Terra (eruptions 2001 to 2003) and Landsat-8 (eruptions 2015-2017).

The aim of this approach is to estimate the lateral spatial heterogeneity of spectral emissivity on ground at known volcanic targets, and to assess whether spaceborne estimates are reliable enough for incorporating experimental laws into the techniques of automated eruption detection and quantitative assessment and monitoring of lava flows.

The refinement of emissivity contributions to the accuracy of actual temperatures, is expected to improve the remote-sensed contributions to mass flux estimates - through the radiant flux proxy, by an appropriate cooling model - whereas relevant rheological parameters (latent heat, vesicularity, and crystals grown percentage) still cannot be estimated from remote, and rely upon known spatial/temporal distributions on ground.

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# Session S23

# Minerals at non-ambient conditions: A Snapshot of the Earth and other planetary bodies

Conveners AND CHAIRPERSONS Paola Comodi (Università di Perugia) Matteo Alvaro (Università di Pavia) Martha Pamato (UCL)

#### Homogeneous solid nucleation in iron and iron-oxygen mixtures at Earth's core conditions

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Keywords: Earth'core, freezing, molecular dynamics.

The formation of the solid inner core is a defining moment in Earth's history. Thermal history models calculate the inner core growth history directly. All current models assume that the inner core nucleates when the melting curve for the liquid iron alloy falls below the core (adiabatic) temperature at Earth's centre. However, freezing of solid from liquid requires the creation of a solid-liquid interface, with an associated free energy barrier. The size of the barrier is determined by the competition between the (negative) volumetric and (positive) interfacial free energy; the top of the barrier corresponds to the critical radius, beyond which crystals will continue to grow. The time required for crystals to reach the critical radius is infinite if the system is at the melting temperature and therefore some undercooling is needed for the system to reach equilibrium with solid as the stable phase below the melting temperature. The key issue is determining whether the required degree of undercooling is consistent with the known size of the inner core. Recently, Huguet et al. (2018) revisited this problem using classical nucleation theory (CNT) and found that an undercooling of ~ 1000 K is needed to bring the waiting time below O(1) Gyrs, but as soon as the core started to freeze the free energy barrier to nucleation would be removed, and so the whole liquid below the melting temperature would freeze, which would correspond to a region much larger than the current size of the inner core. This caused Huguet et al. to label the problem the 'inner core paradox'.

Here I will discuss the major uncertainties and assumptions involved in the application of CNT to inner core nucleation using molecular dynamics simulations conducted at core conditions, and focussing on iron and iron-oxygen alloys. We test the basic validity of CNT at core conditions by calculating the waiting time required to observe freezing events in a suite of simulations and comparing to the CNT prediction. We find that the basic assumptions employed in CNT are supprted by direct simulations, although we predict a slightly lower supercooling requirement of  $\sim$  700 K. Crucially, we also found that a large external perturbation, in the form of a density wave, can drastically reduce the supercooling temperature. However, the requirement of density variations of the order of 10% confine the likelihood of such a perturbation only to a giant impact event.

Huguet, L., Van Orman, J. A., Hauck, S. A., Willard, M. A., (2018): Earth's inner core nucleation paradox. Earth Planet. Sci. Lett., 487, 9-20.

## Mineral-physics constraints on planetary cores: the Fe-FeS and the Fe-FeSi systems

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Keywords: iron alloys, high pressure and high temperature, planetary cores.

The physical properties of iron and iron alloys at high pressure and high temperature are crucial for understanding the structure, chemical composition, evolution, and dynamics of planetary interiors. Indeed, the inner structures of all the telluric planets have a similar layered nature: a central metallic core composed mostly of iron, surrounded by a silicate mantle, and a thin, chemically differentiated crust. However, differences in bulk masses and radii suggest different compositions and different mantle to core size ratios, and imply different pressure and temperature conditions in the center of the various planetary bodies. This also reflects on the solid versus liquid state of the core and on the stable crystalline structure of its solid phase. Such a structural and compositional variability greatly influences the planet's heat budget and internal dynamics, including the occurrence of internal convection, and magnetic field generation.

Among the physical properties that are required to understand planetary cores, density and sound velocities are of primary importance, as these can be directly related to seismological observations (Earth's seismological models, Apollo records for the Moon or incoming results from the InSight mission to Mars). Here I will discuss density and sound velocities at high pressure and high temperature of solid fcc-Fe and liquid Fe-S alloys. These results will be used to model the Moon's core. Concerning the Earth, I will focus on the pressure-volume-temperature relations and sound velocity-density systematics of solid hcp-Fe and hcp-Fe-Si alloys to place constraints on the Si content of the Earth's inner core.

# Measuring changes in crystal structures under compression

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Keywords: coordination polyhedra, high pressure, distortion parameters.

Volume-related parameters of atomic coordinations are useful tools for the analysis of structural changes. For non-regular coordination polyhedra, a determination of the point with the minimum variation of distances to the vertices (the centroid of the coordination) is a necessary prerequisite for a calculation of volume-related parameters. The three parameters that completely describe distortion of a coordination are the eccentricity (displacement of the central atom from the centroid), asphericity (deviation of the surrounding atoms from a common sphere) and volume distortion (deviation of the polyhedron volume from the maximum possible volume of a polyhedron with the same coordination number inscribed inside the same sphere). Furthermore, for a complete understanding of structural changes, not only the distortions of coordination polyhedra, but also of the voids between them, have to be calculated. The voids can be treated the same way as coordination polyhedra, with only two distortion aspects (asphericity and volume distortion). The approach to the study of minerals under pressure will be illustrated by several examples.

# Phase diagrams of minerals at deep Earth conditions: a coupled first principles and computational thermodynamic investigation

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Keywords: phase diagram, deep Earth, computational thermodynamics.

Knowledge of phase diagrams is crucial to predict stability relations, solid-state phase transformations and melting of minerals in planetary interiors. Despite the outstanding progress in computer technology and experimental facilities, thermodynamic properties of deep Earth's minerals are still poorly constrained and their extrapolation at HP-HT conditions is affected by large uncertainties. Furthermore, even the most advanced methods to investigate melting currently display severe limitations that often prevent accurate prediction of phase diagrams and solidus/liquidus phase relations at planetary interior conditions. In this work a novel theoretical framework to predict subsolidus and melting relations by a combination of state-of-the-art *ab initio* calculations for solids, polymer chemistry for silicate liquids and computational thermodynamics for solid-melt equilibria is presented and discussed (Belmonte et al., 2017a). This method allows to compute multi-component phase diagrams in a broad range of P-T conditions, that are in turn used as a source of information to gain new insights on the high-pressure behavior of mineral assemblages in the Earth's interior and to provide physicallyconsistent thermodynamic constraints on both present-day and early Earth melting processes. Application of the above method to binary and ternary systems relevant to the Earth's interior (i.e. MgO-SiO<sub>2</sub>, CaO-SiO<sub>2</sub>, MgO-Al<sub>2</sub>O<sub>2</sub>-SiO<sub>2</sub>) highlights as a first principles Mie-Grüneisen equation of state based on lattice vibrations is able to provide physically-consistent P-V-T relations without any need to rely on empirical parameters or other phenomenological formalisms which could give anomalies or uncontrolled extrapolations at HP-HT (Belmonte, 2017). The most relevant outcomes of this work can be summarized as follows: i) majorite-pyrope garnet and periclase are key to understanding melting relations and solid-state phase changes in the mantle transition zone and lower mantle, respectively, provided that their chemico-physical properties are properly assessed; ii) calculated density changes across the major seismic discontinuities in the Earth's mantle are different from that inferred by geophysical models: this suggests either incomplete dissociation reactions or the occurrence of multiple phase changes in deep mantle aggregates; iii) pressure effects simplify melting relations by drastically reducing the number of minerals with a primary phase field at HP-HT (Belmonte et al., 2017a,b).

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Belmonte, D., Ottonello, G. & Vetuschi Zuccolini, M. (2017a): The system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> under pressure: a computational study of melting relations and phase diagrams. Chem. Geol., 461, 54-64.

Belmonte, D., Ottonello, G. & Vetuschi Zuccolini, M. (2017b): Ab initio-assisted assessment of the CaO-SiO<sub>2</sub> system under pressure. CALPHAD, 59, 12-30.

#### Hydrothermal synthesis of corrensite from Stromboli ash and implications for Mars

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Keywords: Stromboli, ash, hydrothermal alteration.

Understanding processes that occur on the Earth is essential to investigate the processes that rule the planetary geology, since many of the same geological processes occurring on Earth also took place on Mars. Alteration by hydrothermal circulation in the cooling crust and impact-generated hydrothermal alteration have both been proposed as a plausible formation mechanism for 'deep' phyllosilicates on Mars. Indeed, impact induced hydrothermal systems in the volatile-bearing crust of Mars, resulted in various Al/Fe/Mgrich phyllosilicate alteration phases (e.g., Ehlmann et al., 2011). Moreover, as pointed out in a recent study of terrestrial analogs in the Atacama desert (Ruff & Farmer, 2016), hydrothermal environments may have created suitable environments for life and should be a prime target in the search for bio-signatures on Mars. Interestingly, the composition of basaltic ash deposits from Stromboli share some remarkable similarities with Martian rocks. In this contest, the reactions occurring during hydrothermally altered ash from Stromboli (Italy) were studied as a possible analog reactions developed on the Martian crust. The starts sample is trachybasalt in composition and mainly consists of sideromelane glass with crystals of plagioclase, pyroxene and olivine. The hydrothermal experiments were performed at constant pH = 5, pressure of 0.1-50 Mpa and temperature from 150 °C to 350 °C, with runs length of 5 and 31 days. The XRPD patterns indicate that the reactions at temperature under 200 °C, at 0.1 MPa were inhibited. In addition, with increasing pressure (from 0.1 MPa to 50 MPa), at 350 °C, a complete reaction takes place producing corrensite crystals (mixed-layered clays) (Mg,Fe)<sub>9</sub>(Si,Al)<sub>8</sub>O<sub>20</sub>(OH)<sub>10</sub> nH<sub>2</sub>O. XRPD patterns indicate that corrensite crystallizes mainly at the expense of plagioclase. SEM observations show that corrensite occur in thin wavy lamellar sheets from 1 to 8 µm in width. The DTG curve shows two separate steps of dehydration: the former at 160 °C and the latter at 676 °C associated with the breakdown of the mineral structure. As recent studies (e.g., Carter et al., 2013) have confirmed the presence of corrensite on the surface of Mars the results obtained could shed new light on the hydrothermal synthesis conditions and process encountered during evolution of this planet.

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#### Raman approach to evaluate the strain state of synthetic host-inclusion pair

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Keywords: inclusion, strain, elastic geobarometry.

Elastic geobarometry makes use of the contrast in elastic proprieties between host inclusion pairs to determine entrapment pressures for the inclusions. The theoretical basis has been developed extensively in the past few years, but an experimental validation and assessment of the calculated P and T of entrapment is still required. Such validation cannot come from measurements on inclusions in natural rocks as we do not know the exact P and T of entrapment. However, synthetic host-inclusion pairs can be produced using laboratory apparatus for high-P and T experiments (e.g. piston cylinder). On the samples recovered from high P-T experiments, the inclusion pressure can be determined using Raman spectroscopy or X-ray diffraction combined with knowledge of the elastic behavior of the inclusion mineral. To validate the theoretical model for elastic geobarometry on simple synthetic systems, we performed several experiments using a piston cylinder apparatus exploring ranges of pressures from 1 to 3 GPa and temperatures from 700 to 1200 °C following two different protocols. In one case we used one monocrystalline garnet rod as a seed crystal to favor epitaxial growth of newly-formed garnet while trapping inclusion phases mixed into a glass powder. The second protocol relies on growing the host and the inclusions simultaneously using a mix of oxides. Following these protocols, we produced many quartz inclusions trapped in garnet hosts. To avoid issues regarding the geometry of the system (e.g. shape of the inclusion and the proximity to the surface or other inclusions) that may affect the residual strain on the inclusion (Mazzucchelli et al 2018) we selected isolated inclusions in a fracturefree garnet host, with radius at least three times larger than that of the inclusion. We performed micro-Raman measurements to determine the shift of several Raman bands and used the calibration (Murri et al., 2018) to determine the strains still acting on the various quartz inclusions. This approach allowed us to determine for the first time the full strain state still acting on inclusions trapped in their host after recovery from synthesis experiments in a wide range of P and T conditions.

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Mazzucchelli, M.L., Burnley, P., Angel, R.J., Morganti, S., Domeneghetti, M.C., Nestola, F. & Alvaro M. (2018): Elastic geothermobarometry: Corrections for the geometry of the host-inclusion system. Geology, 46(3), 231-234.

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# The smaller the stronger - The more yielding the more obstinate: Guidelines to identify preserved mineral inclusions

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Keywords: Brittle fracture, Mechanical strength, Plastic deformation.

Fluid inclusions are known to be formed at pressures reaching some tens of kilobars. The solid matrix encompassing the fluid filled cavity experiences decompression as a consequence of uplift processes such as eruptions. This event may prompt the mechanical failure of the host-mineral matrix through either decrepitation or stretching, depending on a brittle or ductile mechanism of matrix failure, respectively (Bodnar, 2003).

Laboratory experiments performed on synthetic inclusions show that the decrepitation temperature is strongly size dependent, with smaller cavities observed to decrepitate at higher temperatures. On the other hand, natural inclusions which undergo migration through a pressure gradient are always found intact below a critical size (Roedder, 1984).

In this paper, we model fluid inclusions as spherical cavities in a continuous elastic-plastic medium. Under these conditions, the differential stress applied in the matrix has a cubic dependence on 1/r, where r is the radius of the cavity.

The maximum differential stress concentrates at the cavity/matrix interface. For a matrix with a brittle response, if a non-local stress approach to fracturing is adopted, we demonstrated the fundamental prediction that the decrepitation phenomenon is characterized by a threshold size, and a threshold internal pressure of the cavity, below which decrepitation would not be allowed. The order of magnitude of the decrepitation threshold size is 1  $\mu$ m for the analysed datasets of quartz and olivine inclusions (Campione et al., 2015). For a matrix with a ductile behaviour, plastic yield prevents critical differential stresses to be reached during uplift. However, substantial volumetric expansion starts if a threshold overpressure is reached. This overpressure influences the maximum value of the inclusion pressure one might expect for a specific matrix, and the inferred depth of magma storage levels (Campione, 2018).

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# Investigating reflectance properties of space weathered silicates: effect of swift heavy ion irradiation

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Keywords: Space weathering, amorphisation, reflectance spectroscopy.

Space weathering strongly modifies the surface of Mercury, affecting the characteristics of minerals and rocks, due to the proximity of the Sun and the absence of atmosphere. Space weathering interests in different way the material present on the surface, inducing deformation and vacancies in the crystal lattice (see Domingue et al., 2014). Thus, spectral properties, from the VNIR to the MIR, can be affected by the environment.

MESSENGER mission results highlighted that Mercury's surface is mainly volcanic in origin, spectrally variegate. XRS and GRS data (Solomon et al., 2007) indicated that principal minerals in the crust can be iron-free olivine (ol) and pyroxene, plagioclase (pl), quartz, and in minor abundance, corundum, nepheline (neph), and Mg-Ca sulfides (e.g. Vander Kaaden et al., 2017).

Here, we present a spectral study of swift heavy ion irradiation of three silicates, ol, neph, and pl as a simulation of heavy ion irradiation of Mercury. Three chips of each mineral were irradiated at GANIL-IRRSUD (France) with 88 MeV <sup>129</sup>Xe<sup>23+</sup> ions with fluences of 10<sup>11</sup>, 10<sup>12</sup> and 10<sup>13</sup> ions/cm<sup>2</sup> Spectra were acquired from the VNIR to the MIR (0.4-15 mm) on the unirradiated and irradiated targets, using bidirectional or confocal reflectance (more detail can be seen at Carli et al., 2018).

Preliminary analyses show that: 1) in the NIR reflectance increases and it decreases in the VIS, with a consequent reddening, with increasing the ion fluence; 2) in the MIR the Christiansen Feature has no evident shift, whereas the Reststrahlen band peaks are shifted with increasing fluence up to highest fluence, where the samples show signs of amorphisation.

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#### The high pressure behavior of ternary sulphides from the sulphosalt family

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Keywords: sulphosalts, high pressure, EOS.

Sulphosalts (Me+,Me<sup>2+</sup>,etc.)x[(Bi, Sb, As)<sup>3+</sup>, Te<sup>4+</sup>]y[(S, Se, Te)<sup>2-</sup>] represent interesting material both for earth and applied sciences. They could represent new technological materials with specific optical, magnetic and electric properties, e.g. their band gaps have values interesting for solar cell technology. For earth sciences, they represent low cost material for metal extraction and they have interesting structure types based on high coordination numbers (six and more) which are consider the low P equivalents of high P silicate minerals assumed to be common in the deep earth. Moreover, due to the presence of Lone Electron Pairs (LEP) in metalloids and in some metals, their crystal structures' evolution at varying P-T conditions have very interesting peculiarities.

New data on emplectite isotypic series ( $CuSbS_2$ - $CuBiS_2$ ) and lillianite ( $Pb_3Bi_2S_6$ ) collected with single crystal X-ray diffraction data from synchrotron radiation at different P are presented together with those from recent litterature (Periotto et al. 2012 and reference therein) to give a preliminary overview of ternary sulphosalts behaviour.

The sulphosalts investigated so far are relatively soft, with the  $K_0$  values changing from 27 in  $Sb_2S_3$  (Lundegaard et al. 2003) to 55 in  $CuBiS_2$ , whereas the K' values change from 3.9 to 7.9, with the well known inverse correlation between K' and Ko maintained in sulphosalts, too. A general relationship between the metal/sulfur atomic ratio and K', as well as the metal atom sizes and  $K_0$  is present. The LEP activity of Sb, Bi and Pb affects the structures in different way. In emplectite isotypic series, Sb shows larger stereochemical activity than Bi, whereas in lillianite LEPs of Pb and Bi show a moderate stereo chemical activity until the phase transition. At P over 11 GPa for chalcostibite (Comodi et al., 2018) and around 4 GPa for lillianite (Olsen et al., 2008), phase transitions occur, as indicated by a step-wise change in unit cell parameters and in the space groups (in calcostibite from *Pnma* to *P21* and in lillianite from *Bbmm to Pbnm*). A phase transition is estimated to occur in emplectite at P higher than 9 GPa as indicated by additional reflections violating the *Pnma* space group. The phase transitions are of first order, anisotropic, produce new structures more compact and denser than the low P phases with an increase of the average CN of metals and semimetals. All observed phase transitions are displacive with a reorganization of the archetypal modules, reversible and the single crystals are preserved after the transitions, an aspect that might be important for specific technological applications.

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# Emissivity and reflectance measurement at low and high T of different hydrous salts: a tool to study the surface of the icy planets

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Keywords: icy planetary bodies, reflectance, emissivity.

Jupiter's moons, Europa in particular, have attracted the scientific investigation due to the likely presence of oceans which is consider as the most promising place to look for environment suitable for life. Jia et al. (2108), re-analyzing data from Galileo mission (which collected several information in the period 1995-2003) and that from Hubble telescope, provide strong evidences of the presence of vapour plumes at Europa. The new data increase the interest toward the two missions currently under development aimed at ocean worlds and planned for the next decade: the NASA's Europa Clipper and ESA's JUICE missions. Several questions remain open about the planetary oceans: where are they localized, how are they maintained, what are their characteristics, how they affect the behaviour of the planetary bodies and, of course, are they habitable?

One way to contribute to solve these questions is to describe in detail the surface ice composition through analysis of exiting spacecraft data and telescopic observations. The composition of Europa's non-ice surface material is assumed to be mixtures of sulfuric acid hydrates, brines, and salt hydrates (Hanley et al., 2016; Dalton III et al., 2003). However, the existing data for comparison with planetary observations are usually restricted to small spectral ranges and collected only at room T. In this study, the emissivity and reflectance spectra of a selected group of minerals were collected at low and high T to investigate the role of both chemical substitutions and the amount of water molecules on spectral features. The samples were: thenardite Na<sub>2</sub>SO<sub>4</sub>, arcanite K<sub>2</sub>SO<sub>4</sub>, barite BaSO<sub>4</sub>, gypsum CaSO<sub>4</sub>·2H<sub>2</sub>O, kieserite MgSO<sub>4</sub>· H<sub>2</sub>O, pentahydrite MgSO<sub>4</sub>·5H<sub>2</sub>O, epsomite MgSO<sub>4</sub>·7H<sub>2</sub>O, halite NaCl, silvite KCl, blodite Na<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, loweite Na<sub>12</sub>Mg<sub>7</sub>(SO<sub>4</sub>)<sub>13</sub>·15H<sub>2</sub>O, kainite KMg(SO<sub>4</sub>)·Cl·3H<sub>2</sub>O, carnallite KMgCl<sub>3</sub>·6H<sub>2</sub>O) and polyhalite K<sub>2</sub>Ca<sub>2</sub>Mg(SO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O.

Two sets of measurements were collected: a) Emissivity, in the 1-16 mm spectral range, in a purging environment at different T up to 130 °C and under vacuum between 200 and 500 °C; b) Reflectance in vacuum environment at room T and at -80 °C. All samples were recovered after the heating and freezing cycle measurements and were characterized by using electron microprobe and X-ray diffraction.

The final aim of the project is to improve the spectral library of possible *non-ice* materials and to associate the structural and chemical changes to selected bands in the emissivity and reflectance spectra, on a large spectral range. Moreover, the spectral evolution studied in a wide T range, from -80 °C to around 500°C allows the understanding of the T dependence gradient of different spectral bands.

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# Mechanical Brazil twins and {1011} amorphous lamellae in quartz: indicators of low-pressure shock metamorphism

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Keywords: quartz, brazil twins, planar deformation features.

The largest volume of rocks involved in meteorite impacts normally undergoes pressures below 15-20 GPa. Because of this, the shock signature of quartz at low-pressure regimes (<17.5 GPa), is a key feature that can be used to identify impact craters of any age, and preservation. However, recognizing the shock signature of quarts has proven difficult, particularly below 10 GPa (e.g., Poelchau and Kenkmann, 2011).

In the framework of the MEMIN program, shock recovery experiments on sandstone and quartzite were performed in order to assess the low-pressure response of quartz at low-pressure regimes (5 to 17.5 GPa; Kowitz et al., 2016). These samples were analyzed through transmission electron microscopic (TEM), to detect defects at the nanoscale.

Planar deformation features (PDFs) were recognized in all the samples, including sandstone and quartzite respectively shocked at 5 and 7.5 GPa. That lowers the so far reported pressure range of formation of PDFs (Kowitz et al., 2016). PDFs are parallel to the rhombohedral planes or to the basal plane (0001). PDFs parallel to the rhombohedral planes are amorphous and mostly parallel to the {1011} planes. The (0001) lamellae show the typical fringe patterns and partial dislocations known for mechanical Brazil twins (BT). Altogether, {1011} lamellae and BT represent two-third of PDFs.

The occurrence of mechanical BT constrains the behavior of quartz at low-pressure shock regimes. Indeed, their formation requires that high shear stress ( $\sim 2$  GPa) prevails over the quartz basal plane at moderate temperatures (500-700°C) and pressures > 4 GPa (McLaren et al., 1967). Finally, for the first time, this work shows processes of amorphization of BT. We suggest that the amorphous (0001) lamellae identified optically have been formed as mechanical BT.

This work shows that, the mechanical BT and {1011} amorphous lamellae are the only reliable indicators of low-pressure shock regimes. Thus, in absence of optically visible shock criteria, TEM observations are essential to identify and interpret of planar defects.

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# Thermal Infrared spectroscopy of anorthositic analogues at Mercury-like (non-ambient) temperature conditions

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Keywords: Mercury, emissivity, temperature.

The surface composition of Mercury has been recently reviewed by MErcury Surface, Space Environment, GEochemistry, and Ranging (MESSENGER) findings, which point to low-Fe and Mg-rich basalts as the main constituents (Nittler et al., 2011). This interpretation dismisses the previously assessed widespread presence of more felsic materials - as on the Moon's surface - leaving unfilled the crust petrogenesis of Mercury. Assessing the presence of a differentiated crust on the surface of Mercury is among the intrinsic objectives of the next ESA/ JAXA BepiColombo mission to Mercury, of which Mercury Radiometer and Thermal Imaging Spectrometer (MERTIS, 7-14 µm) will map the surface mineralogical composition of the planet. Due to the vicinity to the Sun and to the rarefied atmosphere, Mercury undergoes to a wide range of surface temperature that depends on latitude and longitude. A complication that occurs during the interpretation of thermal infrared spectra collected along such ranges of daily surface temperatures is the relocation of the band minima depending on the temperature (e.g., Helbert et al., 2013). In addition, the simultaneous presence of different minerals, each one with its characteristic thermal expansion coefficient, results in a more difficult interpretation of the spectra. In this work we examine the spectral variations of linear mixtures of plagioclase and pyroxenes that most likely could be present in the differentiated igneous crust of Mercury, in addition to the T-dependent spectral variations of the single constituents. To this aim we measured the reflectance of the samples at ambient temperature, and their emissivity from 425 K to 725 K. All measurements are conducted in vacuum.

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## The elastic properties of hcp-Fe alloys under the conditions of the Earth's inner core

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Keywords: computational mineral physics, hcp-Fe alloy, inner core.

Although one third of the mass of our planet resides in its metallic core, fundamental properties such as its chemical composition and internal structure remain poorly known. While it is well established that the inner core consists of iron with some alloying lighter element(s), the crystal structure of the iron and the nature and concentrations of the light element(s) involved remain controversial. To date, no candidate composition for the inner core has been able to match both the density and seismic wave velocities observed by seismology. In particular, seismically observed shear waves show unexpectedly low propagation velocities through the inner core. Unfortunately, the extreme conditions of pressure (up to 360 GPa) and temperature (up to 6000 K) required make results from laboratory experiments tricky. An alternative and complementary approach is computational mineral physics, which uses computer simulations of materials at inner core conditions. We find that while binary alloys do not match the observations, there are a range of ternary and quaternary alloys that do match the seismology. Interestingly, carbon is always a necessary component of these alloys, since C has the greatest effect on the elastic moduli. This is the first time that VP, Vs and the density of the inner core have been matched directly with an hcp-Fe alloy.

### Intermediate scapolite: crystal chemistry, structure and behavior at non-ambient (P,T)-conditions

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Keywords: scapolite, space group, pressure.

Scapolites, general formula  $M_4T_{12}O_{24}A$ , are important minerals in metamorphic rocks, ranging from the greenschists to the amphibolite facies, where can act as hosts for volatiles (mainly Cl<sup>-</sup>, CO3<sup>2-</sup> and SO4<sup>2-</sup> anions). From the crystal-chemical point of view, they represent a complex group of minerals, for which three end members have been described: marialite (Na<sub>4</sub>Al<sub>3</sub>Si<sub>9</sub>O<sub>24</sub>Cl), meionite (Ca<sub>4</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>CO<sub>3</sub>) and silvialite (Ca<sub>4</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>SO<sub>4</sub>). Along the marialite-meionite joint, complex substitution mechanisms govern the occurrence of three binary solid solutions (Sokolova & Hawthorne, 2008), which are coupled with intriguing crystallographic features. In fact, in the literature, the members close to the marialite and meionite sides are reported to crystallize in the *I*4/*m* space group, whereas the intermediate members are always reported to share the *P*4,/*n* space group.

In this work, a gem-quality transparent single-crystal of intermediate scapolite ( $(Na_{1.86}Ca_{1.86}K_{0.23}Fe_{0.01})$  ( $Al_{4.36}Si_{7.64}$ )O<sub>24</sub>[ $Cl_{0.48}(CO_3)_{0.48}(SO_4)_{0.01}$ ]) from Madagascar has been investigated by means of both conventional lab and synchrotron X-ray diffraction. Interestingly, all the experimental X-ray diffraction datasets show the occurrence of systematic extinctions compatible with an *I*-centered lattice, which is in contrast to what expected for an intermediate scapolite member.

The high-pressure and high-temperature behaviors of the same intermediate sample of scapolite have also been investigated by means of in situ powder and single-crystal X-ray diffraction, using conventional X-ray sources, at the University of Innsbruck (HT-SCXRD), or synchrotron facilities, at Elettra (Trieste, HT-PXRD) and at ESRF (Grenoble, HP-SCXRD).

The high-*P* evolution of the unit-cell volume of scapolite has been fitted by a III-order Birch-Murnaghan equation of state, which yielded a refined bulk modulus of 70(2) GPa ( $\beta_{\nu_0} = 0.0143(4)$  GPa<sup>-1</sup>). A comparison with the high-pressure behavior of three further members belonging to the marialite-meionite joint (Hazen & Sharp, 1988; Comodi et al., 1990) confirms the control played by the crystal chemistry on the bulk compressibility: at a first approximation, the bulk modulus linearly increases from marialite to meionite. In addition, a displacive phase transition from the *I*4/*m* toward a triclinic polymorph was found to occur at 9.87 GPa.

Preliminary analysis of the high-temperature data revealed a significant anisotropic thermal expansion, which is almost exclusively accommodated in the plane perpendicular to the tetragonal axis, i.e. (hk0).

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#### Spinel+chlorite assemblage forms only at ultrahigh pressures in garnet-hosted inclusions

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Keywords: subduction, oxygen fugacity, multiphase inclusions.

The action of slab-derived fluids on mantle rocks frequently brings about the formation of microcavities in minerals, which represent microenvironments where the interaction between fluid and host mineral is preserved during the whole geological path of the rock. The entrapped fluid and the host matrix constitute a system evolving towards equilibrium under peculiar chemical-physical constraints. By expliciting these constraints through mass conservation laws and stoichiometry relations accounting for the composition of the host mineral and of the initial fluid, and for the presence of a finite fluid-solid interface, we show that cavities in minerals filled with slab-derived fluids can re-equilibrate following a crystallisation mechanism which is not predictable through simple equilibrium arguments holding for open systems (Campione et al., 2017). The occurrence of phases stable at ultrahigh pressure (UHP), such as coesite or microdiamond, has long been considered evidence of precipitation from such fluids at P > 3 GPa. Here, we demonstrate that even a mineral association characterised by phases usually considered stable at relatively low pressure in mantle systems (e.g., spinel + chlorite), would potentially crystallise at UHP by chemical fluid/host interaction.

We will consider as a case study a well-known example of multiphase solid inclusions occurring in the cores of garnets forming orthopyroxenites from the Maowu Ultramafic Complex (Eastern China), interpreted as hybrid rocks resulting from the interaction of previous harzburgites and slab-derived silica-rich liquids (P = 4 GPa, T = 800 °C) at the slab-mantle interface. Malaspina et al. (2015) demonstrated the epitaxial relationship between spinel and garnet, which suggested nucleation of spinel under near-to-equilibrium conditions. On the contrary, hydrous phases (amphiboles, chlorite and ±talc ±phlogopite) nucleate in a non-registered manner and likely under far-from-equilibrium conditions. The epitaxial growth of spinel with respect to garnet and the chlorite rim + water assemblage filling the space between the host garnet and the other inclusion minerals (Malaspina et al., 2017), suggest that spinel and chlorite formed at UHP together with the garnet cores.

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# Phase equilibria and element partitioning of a carbonated oceanic crust at high pressure and temperature

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Keywords: diamond, mantle redox state, deep carbon cycle.

Sublithospheric diamonds contain mineral inclusions like majorite, stishovite, solid carbonates, Na-Al rich phase (NAL) and Ca-ferrite mineral that are all representative of the transition zone and lower mantle. In light of previous experimental studies, these minerals have been interpreted as crystallised during deep subduction of the basaltic oceanic crust and trapped by diamonds that might have formed by redox reactions involving Fe-bearing mineral phases. It is, therefore, important to study mineral phase equilibria at high pressure and temperature at oxygen fugacities where both carbon and carbonate coexist and identify potential redox sensitive minerals able to affect the speciation of carbon.

We performed experiments in the pressure range of  $\sim 12$  and 24 GPa using multi anvil presses available at the Geodynamics Research Centre (GRC) of Ehime University (Matsuyama, Japan), and temperatures between 800 and 1600 °C. Starting materials consisted of synthetic carbonated glass with mid-ocean ridge basalt compositions, amorphous silica, natural magnesite, synthetic clinopyroxene and garnet with eclogitic composition. The oxygen fugacity in our experiments was buffered by a chemical equilibrium like stishovite + dolomite = majorite + diamond + O2 similar to the DCDD buffer proposed by Luth et al. (1993) and studied by Stagno et al. (2015). Iridium was added to the starting mixture to act as redox sensor. Natural kyanite and synthetic garnet glass were used as pressure markers in our experiments.

Preliminary textural and chemical analyses show the coexistence of Na-bearing carbonates and diamonds in all experiments along with Fe-rich majorite, stishovite, rutile, ilmenite but also a majoritic phase with stoichiometry like omphacitic cpx, and a Na, Al bearing phase enriched in Fe. Some of these recovered minerals have compositions similar to those reported for natural minerals included in superdeep diamonds. Interestingly, the stability of Fe-rich majorite and Na, Al bearing phases implies their key role in deep processes such as redox freezing/melting of a subducted oceanic crust limiting, therefore, the transport of carbon at depths of the lower mantle.

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# Elastic properties of Fe-Si-C alloys: Testing the composition of the Earth's inner core

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Keywords: Earth's inner core, Fe-Si-C alloys; high-pressure, sound velocities.

By comparing the elastic properties of relevant materials at pertinent pressure and temperature conditions with seismic properties it is possible to interpret geophysical observations in terms of the chemical and thermal state of the Earth's interior. In the mantle, sound wave velocities can be understood in terms of mineralogical and compositional models, with these models matching the observed velocities to about a percent or so. On the contrary, for the inner core compressional ( $V_p$ ) and, in particular, shear velocities ( $V_s$ ) are observed to be much lower (10-30 %) than those usually inferred from mineral physics.

Recent computer simulations revealed that pure *hcp*-Fe could match the observed sound wave velocities as a result of pre-melting softening of the elastic constants at 360 GPa just before melting (Martorell et al., 2013). However, although the low seismic wave velocities of the core could be explained by this model, the density of pure iron is still too high to match geophysical data, implying that at least one lighter element, if not more, is required to be alloyed to iron in the inner core to account for this deficit. More recently, *ab initio* molecular dynamics calculations revealed a ternary Fe-Si-C alloy satisfying all the observed properties of the inner core (Li et al., 2018). This is the first candidate material that, without any extrapolation, is predicted to match all of the seismic constraints. It is essential, therefore, to validate these calculations experimentally.

In this light, we carried out sound velocity and density measurements on *hcp* Fe-Si-C alloy with 1.6 wt. % Si and 0.7 wt. % C up to ~120 GPa, using inelastic X-ray scattering (IXS) and X-ray diffraction. IXS allows a clear identification of longitudinal aggregate excitations in polycrystalline samples, the direct derivation of  $V_{p}$ , and provide, combined with the measured equations of state, the estimation of  $V_s$ , while the density is directly obtained from the collected diffraction patterns. In this study, we aim to establish precise relations between velocities and density for Fe-Si-C alloys over a wide pressure range, providing a vital experimental validation of the simulations results. Further calculations will be performed at the same P-T conditions of the experiments to complement the experiments and validate the theoretical approach. This research will provide significant advances in our understanding of Earth's core composition, and hence of its origin and evolution.

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Li, Y., Vočadlo, L. & Brodholt, J.P. (2018): The elastic properties of hcp-Fe alloys under the conditions of the Earth's inner core. Earth Planet. Sci. Lett. 493, 118-127.

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# Fingerprinting diamonds growth conditions through the time and temperature dependence of the properties of magnetic inclusions

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Keywords: Magnetic inclusions, Diamonds, Hysteresis.

Complete understanding of the physical and chemical conditions for the formation of diamonds in the Earth's mantle is still one of the most debated issues of geoscience. The determination of the crystallographic properties of mineral inclusions entrapped during the formation and subsequent growth of diamonds has been proved a proper tool to get insights on this topic (Angel et al., 2015). Useful complimentary information can be retrieved when dealing with inclusions showing magnetic ordering (Collinson, 1998; Viddal & Roshko, 2006). Indeed, the magnetic properties of these inclusions have time and temperature dependences resembling the thermodynamic conditions in which the host diamonds grew. However, to reconstruct such information a systematic characterization of magnetic inclusions in diamonds, together with the development of theoretical tools enabling to model their magnetic behaviour, is needed.

Here we first investigate the crystallographic, chemical and magnetic properties of several inclusions present in diamonds from South Africa by means of X-ray diffraction (XRD), Raman spectroscopy (RS) and Alternating Field Gradient Magnetometry (AFGM). XRD and RS analyses show that in our samples magnetic inclusions appear mainly as magnetite and hematite powders, with typical size of ~50-100  $\mu$ m and mass of few micrograms. The hysteresis loops and first-order reversal curves (FORCs) detected for magnetite inclusions through AFGM measurements show that magnetite grains behave as single-domain (SD) particles having isothermal remanent magnetic moments  $m_{IRM}$ ~1 nAm<sup>2</sup> and coercivities  $B_C$ ~5 mT.

We then investigate the magnetization processes undergone by the magnetic inclusions within the framework of the Preisach model of hysteresis (Hejda & Zelinka, 1990). By treating each SD particle as a Preisach bistable unit with its own bias  $(H_b)$  and coercive field  $(H_c)$  and by using the FORCs experimental data we determine the Preisach distribution  $\rho$   $(H_{b1} H_c)$  of the bistable units composing the samples. We finally use  $\rho$   $(H_{b1} H_c)$  to simulate numerically the hysteresis loops observed in the inclusions, by analyzing in particular how temperature and time relaxation effects affect their behaviour.

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# Synthesis of majorite from omphacitic glass at deep mantle conditions sheds light on the rheology of the subducting oceanic crust

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Keywords: omphacite, majorite, multi anvil press.

The transport of chemical elements through subduction into the Earth's transition zone and lower mantle is strongly affected by the stability of mineral phases at high pressure that, in turn, controls the rheology of the subducting slab. During subduction of the oceanic crust, clinopyroxene (Cpx) reacts with coexisting garnet to form majorite. However, the slow solid-state diffusion associated with this reaction could cause metastable Cpx to be stable up to P and T conditions where it may alternatively decompose to form lower mantle mineral assemblages with important implications for the density of the subducted oceanic crust. Previous experimental studies on the stability of omphacitic Cpx as a function of pressure showed that decomposition occurs to an assemblage of majorite + Ca-perovskite + stishovite, or formation of an unknown post-clinopyroxene phase. However, experiments were performed at the high temperatures of the convecting mantle rather than slab thermal regimes.

Here, we discuss recent results of multi anvil experiments on the crystallization products of synthetic omphacitic glass at  $\sim$ 18 and  $\sim$ 25 GPa and 1000 °C to simulate *P*-*T* regimes of cold subduction. Synthesis runs were carried out using the Walker-type multi anvil press available at the National Institute of Geophysics and Volcanology (INGV) in Rome. The recovered samples were analyzed by field-emission scanning electron microscopy, powder X-ray diffraction and Raman spectroscopy for chemical and textural characterization. Single crystal X-ray diffraction on selected grains allowed to study in more detail the structure of the recovered minerals.

Our results show evidence of direct crystallization of Na-, Si-rich majorite in contrast with the generally proposed formation of high-pressure phases like Ca-perovskite, Mg-perovskite (bridgmanite) and stishovite. To understand the effect of the Cpx  $\rightarrow$  Na,Si-rich transformation on the rheology of the subducted slab, we used our results to model the density, longitudinal ( $V_p$ ) and shear ( $V_s$ ) wave velocities of mid-ocean ridge basalt (MORB) at the pressures of the mantle transition region using elastic parameters of major minerals available in the literature.

This study provides the evidence that an increase in pressure during cold subduction of a clinopyroxenerich portions of the slab results in majorite crystallization through isochemical transformation, which causes an increase in local density by 6% favoring, therefore, the continued floating of the slab.

# Raman on R3+ bearing pyroxenes: a clue to interpret mantle xenoliths from different geodynamic environments?

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Keywords: Al-pyroxenes, raman pectroscopy, high pressure environments.

Crystallographic and spectral analysis of the mineral phases has proved effective to characterize the geological environment of a given mineral assemblage (Princivalle et al 2000). Here we will provide preliminary results on an investigation taking advantage of Raman spectroscopy.

Raman analysis of pyroxenes is a powerful technique to perform serial analysis of their composition and structural state. Changes in peak position of the larger peaks was related to the composition in quadrilateral pyroxenes, either augite, pigeonite and orthopyroxene (Huang et al. 2000, Tribaudino et al. 2011). However in natural pyroxenes, mostly in those for higher pressure environments, trivalent cations like Al,  $Fe_3$ + and  $Cr_3$ + are major constituents, and their presence can be concealed.

Here we investigated a series of natural and synthetic pyroxenes, containing Al, Cr and Fe<sub>3</sub>+. Synthetic pyroxenes were taken from pyroxenes in the CMAS system previously obtained by piston cylinder synthesis at P = 2 GPa and T=1350 - 1430 °C (Tribaudino and Bruno 1993). The compositions of the synthetic pyroxenes fall either in the two pyroxene field in the spinel lherzolite compositions or along the CaMgSi<sub>2</sub>O6-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>, diopside-Ca-Tschermak join. Natural pyroxenes come from a collection of Cr-diopsides from mantle xenoliths from northern (Waw-En-Namus, Libya; Bou-Ibalrhatene and Tafraoute, Morocco) and central Africa (Nyos and Barombi maars, Cameroon). These mantle xenoliths were extracted from mantle domains underlying a metacraton (Libya), a pericraton (Morocco), and a Pan-African mobile belt (Cameroon). They usually have high R3+ content and low Ca.

Raman spectra were measured by blue laser source (473 nm), and for each spectrum the peak position and broadening of the main peaks was reported. The results on synthetic pyroxenes were used as a benchmark to ascertain the differences with natural ones, and to the subsequent analysis relating Raman data with the geodynamical environment of the natural pyroxenes.

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# Fluid-mineral interactions at high-pressure/high-temperature conditions: experiments on the oxidation of graphite and amorphous carbon to carbon dioxide in aqueous fluids at 1-3 GPa and 800°C

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Keywords: subduction, oceanic lithosphere, fluid-mineral interactions.

Subduction of the oceanic lithosphere and its sedimentary cover is accompanied by devolatilization processes, which provide an efficient way to recycle volatiles back to the mantle wedge and, ultimately, to the Earth's surface. CO<sub>2</sub> removal through aqueous dissolution of carbonates occurring in altered oceanic lithosphere and its sedimentary cover has been suggested by thermodynamic models but the experimental data base remains very sparse. Graphite has been considered a refractory sink of carbon in the subducting slab, owing to its lower solubility in aqueous fluids and melts compared to carbonates. However, experimental studies (Tumiati et al. 2017) suggest that in complex systems the silica component derived from the dissolution of promotes the oxidation of graphite to CO<sub>2</sub>, thus controlling the composition of deep COH fluids in particular enhancing their CO<sub>2</sub> content when compared to SiO<sub>2</sub>-free systems. In this contribution, we will focus on the role of graphite crystallinity in the carbon dissolution process. We provide comprehensive experimental constraints on the volatile composition of high-pressure aqueous fluids interacting at 1-3 GPa and 800°C either with graphite or amorphous (glassy) carbon at controlled redox conditions, buffered by using the double-capsule technique and both the nickel-nickel oxide (NNO) and the fayalite-magnetite-quartz (FMQ) buffers ( $\Delta$ FMQ  $\approx -0.5$ ). Solid carbon phases were analyzed both by X-ray diffraction and Raman spectroscopy. Experimental fluids were analyzed for their volatile COH composition by quadrupole mass spectrometry (QMS). Measured data were compared to thermodynamic modeling results. Our results suggest that amorphous carbon is more susceptible to oxidation than crystalline graphite at constant P, T and fO<sub>2</sub>. Therefore, the interaction of deep aqueous fluids and rocks containing graphite or organic matter characterized by a low degree of crystallinity provides a new mechanism for enhancing the CO<sub>2</sub> content of fluids and the deep carbon removal from the downgoing slab.

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#### A novel approach to determine accurate Equations of State for zircon and rutile

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#### Keywords: Zircon, Rutile, Equation of State.

Zircon (ZrSiO<sub>4</sub>) and rutile (TiO<sub>2</sub>) are common inclusions entrapped in garnet hosts from metamorphic rocks. They may preserve remnant strains when measured at room- conditions. Accurate equations of state (EoS) are required to interpret their remnant strains in terms of entrapment conditions (e.g. Angel et al., 2017). Zircon and rutile are very stiff minerals, so obtaining reliable values of their isothermal bulk moduli ( $K_{70}$ ) and pressure derivatives (K') from P-V data alone is problematic. As a consequence, the EoS parameters reported in the literature for zircon and rutile are extremely variable. The elastic moduli can be better constrained by using a thermal-pressure model with no extra parameters to fit the high-temperature volume data, and by simultaneous refining the EoS to direct measurements of bulk moduli (Milani et al., 2017).

We reassessed the available literature data for zircon and rutile in order to derive their EoS parameters. We fitted the data for zircon with a Birch-Murnaghan 3<sup>rd</sup>-order (BM3) EoS combined with a Holland-Powell thermal-pressure model. We restricted the datasets to 5 GPa and 730 °C to avoid the influence of the zircon-reidite phase transition. We obtained  $K_{T0} = 225(2)$  GPa, K' = 6.5 (fixed),  $\alpha V_0 = 1.068(19) \times 10^{-50}$ C<sup>-1</sup> and  $\partial K/\partial T = -0.0155(3)$  GPa/°C. The data for rutile were fitted by a BM3 EoS combined with a Mie-Grüneisen-Debye thermal-pressure model:  $K_{T0} = 205$  GPa (fixed), K' = 8.8(3),  $\alpha V_0 = 2.487 \times 10^{-50}$ C<sup>-1</sup>,  $\partial K/\partial T = -0.040(1)$  GPa/°C.

Our zircon EoS suggests that zircon inclusions in garnets will exhibit positive remnant strains that differ sufficiently to distinguish entrapment at different metamorphic stages. On the contrary, rutile inclusions in garnets should exhibit negative remnant strains thus making rutile unreliable for elastic geobarometry.

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# Session S24

# Geomaterials: Nature, properties and technology

Conveners AND CHAIRPERSONS Francesco Di Benedetto (Università di Firenze) Rocco Laviano (Università di Bari) Paolo Lotti (Università di Milano)

# New spectroscopic and diffraction data to solve the vanadium-doped zircon pigment conundrum

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Keywords: Colour, Crystal structure, EPR and optical spectra.

The literature picture on the V-doped zircon pigment offers a puzzling situation with unanswered questions about the origin of turquoise colour. In this study, new diffraction (XRPD) and spectroscopic (EPR, EAS) data were obtained on four industrial pigments, which differ from those of previous investigations for their much higher vanadium content. The extended range of composition investigated, by merging literature and new experimental results, allows to resume data interpretation and to shed light on the V-doped zircon conundrum. Vanadium occurs as tetrahedrally-coordinated V<sup>4+</sup> at the interstitial site 16g of the zircon crystalline lattice, as indicated by the optical and EPR features, as well as V-O bond distance increasing with vanadium content (XRPD). EPR spectra at 5 K exhibit a structured multiplet attributed to V<sup>4+</sup> (isolated ion) and an exchange-narrowed line likely resulting by clustering of V<sup>4+</sup> ions. The intensity of optical bands is stronger in samples where EPR predicts the occurrence of V<sup>4+</sup> clusters. However, the turquoise colour stems from the window of transmitted green-bluish light, which depends on both the tail of the main optical band (<sup>2</sup>B $\leftarrow$ <sup>2</sup>A) and the onset of charge transfer phenomena. Small variations in these two bands readily turn into a chromatic shift from light blue to green. Conditions affecting the pigment colour are discussed by structural, spectroscopic and technological viewpoints, addressing repercussions on the industrial synthesis of V-doped zircon.

### Insights on Etna anthropic cavities: mineralogical investigations of Ghiara

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Keywords: local building material, Etna paleo-soils, X ray diffraction analyses.

The aim of this work is to focus on mineralogical transformations occurring during the heating process of Etna's lava flows on paleo-soils.

Ghiara is the local name of these paleo-soils whose main feature is the intense reddish colour. The ghiara was extracted for long time in anthropic cavities on the slopes of Etna because it was widely used in XVIII-XIX centuries in Catania (Sicily) architecture as aggregate in mortars principally for the hydraulic features comparable with those of pozzolana (Belfiore et al., 2010) and for its colour.

In this work, we considered a ghiara section of an anthropic cavity, located in the district Castagneto of the Municipality of Nicolosi (Catania, Italy), excavated below the lava flow of 1408, in which we sampled two different ghiara samples: one, in the core section and characterized by its typical reddish colour and the second one in yellow tones located in the top of the ghiara section close to the lava contact. The mineralogical analysis was performed by mean of XRD. The quantitative analysis of crystalline and amorphous phases was obtained by mean of Rietveld calculation. Furthermore Raman spectrometry was used to give complementary information about the mineralogical composition.

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# A petrographic contribution to the characterization of the ornamental stones in the framework of the design and interior luxury furnishings

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Keywords: commercial marbles, stone blocks and slabs, petro-physical characterization.

During the last years, the search of ornamental stones used for interior furnishings such as tables, claddings and floors, has becoming more and more important. The so-called "marbles" in the commercial world comprise all the soft (minerals in the Mohs scale between 3 and 4) and polished stones. This commercial classification is very different with respect to the petrographic constraints considering marbles s.s. only carbonate-bearing metamorphic rocks. The present work started through a collaboration between the Spin Off Geo.In.Tech. s.r.l. of the University of Urbino and the enterprise S2 S.p.a. (Fermignano, Italy), this latter producing manufacts for interior design using highly-prized ornamental stones, for some important brands. In particular, a PhD project (Eureka grant) is ongoing, financially supported by the University of Urbino, Regione Marche and S2 S.p.a., mainly focused on several "marble" lithotypes from districts of the Apuane Alps, Spain and Tunisia (Carmignani et al. 2007; Gosálbez et al. 1999; Gaied et al. 2000). Despite of the aesthetic aspect of the ornamental stones (i.e. colour, geometric texture of the veins and minerals) actually represents the main feature required by the interior designers and ordering customers, petro-physical characterization of the more employed "marbles" will contribute to give other information of paramount importance. The knowledge of the commercial availability of "marbles", both as dimension blocks and/or slabs and suggestions for other possible areas of exploitation of stones with the required aesthetic and physical-mechanical qualities will represent a very useful tool for the organization of the manufacturing production of the enterprise. According to the technical and commercial need of the enterprise and requests by the ordering customers, detailed data sheet for each ornamental stone will compiled. In this way, taking into account the available literature data, we also performed new mineral-petrographic observations by thin section studies and a series of analyses such as SEM-EDAX, X-ray diffractometry, geochemistry, porosity and flexural and compressive strengths. In addition, as the main production of S2 S.p.a. is oriented to manufacture using slabs, it will be very important to define the best worked thickness for each employed lithotype with respect the size of the designed manufact.

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#### Highly-porous light-weight bricks produced recycling organic waste

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Keywords: Porous bricks, Waste recycling, Thermal insulation.

Under the motivation (<u>https://ec.europa.eu/programmes/horizon2020/</u>) of the Horizon2020 program, increasing efforts have been addressed in recent years to the introduction of sustainable products into the marketplace and enhancing awareness on eco-labelling, promoting environmental protection, human health, and supporting sustainable development.

Waste products generated by industry and other human activities may represent a new primary resource if reused in the production process, thus saving primary geo-resources, reducing manufacturing costs, and limiting extension of waste deposits, all pressing priorities for our society. Moreover, the growing demand of low cost and highly-porous bricks in building construction materials has provided improvement in thermal insulation of the final product. From literature, organic-type additives are the most frequently used as poreforming agents because they combust during the firing process of brick production.

In this work, residues from wine production were used to produced new highly-porous light-weight bricks. Following a multi-analytical approach, pores formed from this pore-forming agent were investigated also in terms of the properties they confer to this new type of bricks.

Here we present the preliminary results on mineralogical evolution and physical properties of the experimental brick type obtained using clay materials chemically rich in SiO<sub>2</sub> (57.77 wt.%) and Al<sub>2</sub>O<sub>3</sub> (14.14 wt.%), where 10 % (vol.) of dry milled grapes were added with a grain-size up to 2 mm. Due to the large dimension of part of the pores, porosity was explored both by hydric texts and image analysis at the scanning electron microscope on three differently oriented large sections (4.5 x 3 cm<sup>2</sup>). Thermal insulation analysis was here interpreted in relation to the pore volume and distribution. All the data were compared with those obtained from standard bricks produced using the same base clay. Grapes combustion, indeed, increases the porosity of the final product both in terms of total efficient porosity (%) and in pore dimensions, resulting in enhanced thermal insulation properties. Large size of pores, moreover, favors a good durability moderating possible residual crystals trapped from salt solutions and damages caused by increased volume of ice when in freeze-thaw conditions.

These characteristics and valuable aesthetic properties bode assessments for a possible implementation of the new mix into the market.

#### High-temperature behavior and dehydration of the natural borate colemanite

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Keywords: colemanite, temperature, dehydration.

Colemanite,  $CaB_3O_4(OH)_3 \times H_2O$ , is the most common natural hydrous calcium borate and one of the most important mineral commodities for boron. It is mainly extracted from Turkish deposits, which form from relatively diluted waters of lacustrine basins, hosted in continental semi-arid to arid environments and fed by B-rich hydrothermal springs related to a local volcanic activity (e.g. Helvaci & Alonso, 2000). Due to its common occurrence in waste rocks at extraction sites, several studies have been focused in the recent past on the exploitation of colemanite as raw material, for example as an additive in the production of lightweight cements (Targan et al., 2003) or radiation shielding materials (Glinicki et al., 2018). However, despite the utilizations of colemanite, we still have only a partial knowledge of the high-temperature behavior of this mineral compound.

In this study, we investigated the high-temperature behavior of a natural sample of colemanite from the Bigadiç deposit (Turkey), by means of in situ powder synchrotron X-ray diffraction, performed at the MCX beamline of Elettra (Trieste, Italy), using a hot blower device.

The refined unit-cell parameters show a significantly anisotropic thermal expansion, which is only accommodated along the **b** and **c** crystallographic axes, whereas the **a** axis, corresponding to the direction of the chains of B-coordination polyhedra, is almost unaffected. Between 275 and 325 °C, a reduction in the unit-cell volume and a decrease in the refined occupancy of the  $H_2O$ -oxygen site, reveal the occurrence of a dehydration phenomeno, which is followed by a complete and irreversible amorphization between 325 and 375 °C.

Merging the *V*-*T* data of this experiment with those obtained in a previous low-*T* experiment on the same natural sample (Lotti et al., 2018), a thermal Berman-type equation of state was refined in the range from -171 to 250 °C (104-525 K), yielding a thermal expansion coefficient at ambient-*T* ( $a_{V298K}$ ) of 4.5(1)×10<sup>-5</sup> K<sup>-1</sup> and  $a_1 = 5.7(8) \times 10^{-8}$  K<sup>-2</sup>.

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# Affinity with Rare Earth Elements of a synthetic Cu-Al-SO<sub>4</sub> Layered Double Hydroxide analogous to woodwardite

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Keywords: Woodwardite, Layered Double Hydroxides, Rare Earth Elements.

Woodwardite is a member of the hydrotalcite group (Mills et al., 2012), also known as Layered Double Hydroxides (LDH) or anionic clays, due to the capacity of these compounds to sorb and exchange anions. Minerals of the hydrotalcite supergroup are layered materials with brucite-type layers, where a trivalent cation partially substitutes a divalent cation, generating a net positive charge balanced by an anionic species in the interlayer. The resulting general formula is  $M^{2+}_{1,x}M^{3+}(A^{z-})_{x/2}(OH)_2 \cdot nH_2O$ . In the case of woodwardite,  $M^{2+} = Cu$ ,  $M^{3+} = Al$ , and  $A^{z-} = SO_4^{-2}$ . Thanks to the high versatility of the structure and their low synthesis cost, LDH are receiving an increasing attention in the last decades. A large variety of physicochemical properties can be easily tailored for many different specific applications. One of the application fields of LDHs is their precipitation from metal-rich solutions for scavenging metals from water solutions (Jaiswal et al., 2014). This use could be of interest for mine-waste waters, which are usually quite enriched in metals. In the precipitates from the abandoned Cu mine of Libiola (Northwest Italy) woodwardite presence is linked with high concentrations or Rare Earth Elements (REEs), such as Y (up to 600 mg kg<sup>-1</sup>), Ce, Nd (up to 200 mg kg<sup>-1</sup>), Gd, and Dy (up to 100 mg kg<sup>-1</sup>). The aim of our work was to evaluate the Cu-Al-SO<sub>4</sub> LDH (analogous to woodwardite) potential to concentrate REEs from solutions. With this purpose we performed syntheses in solutions enriched in both light (La, Ce, and Nd) and heavy (Y and Gd) REEs.

The material obtained from the synthesis had poor crystallinity, turbostratic structure, and consisted of nanoscopic crystallites. The incorporation of REEs in the LDH structure led to an increase of the *a* cell parameter. The concentration of REEs in the solid fraction was in the range of 3.5-8 wt %, showing a good affinity between the synthetic LDH and REEs. The only exception was La, which formed segregated phases. As a general rule, heavy REEs showed a higher affinity than the light REEs, probably because of their lower ionic radius. Increasing the pH in the synthesis routine led to an increase of REEs incorporated by the LDH, especially heavy REEs, but caused the oxidation of Ce (from 3+ to 4+) with the consequent formation of ceria. The REE-doped Cu-Al LDHs could be used as a precursor in the production of Cu- and REE-containing oxides through thermal decomposition. Due to its ion-exchange properties, the REE-activated synthetic LDH was also a promising material for Li batteries.

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#### Feldspathic fluxes for ceramics: a global view at sourcing and composition

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Keywords: ceramic, ore deposits, raw materials.

Feldspathic fluxes are fundamental ingredients of many ceramic products, but a global view at the geological sources actually exploited by industry and the lithologies occurring in these deposits is lacking. This contribution reviews the sourcing and composition of feldspathic raw materials (and additional fluxes based on sericite, talc and further low melting minerals) used by or proposed to the ceramic industry. It follows a previous analysis of production trends and market dynamics (Dondi, 2018). A large set of data (about 1400 deposits in 75 countries and over 1300 chemical analyses) was collected from literature and industrial information, critically assessed and elaborated to get an exhaustive picture of deposits and composition of both raw and beneficiated fluxes. Overall, the main sources are granitic suites, including acid differentiates (pegmatites and aplites) and the corresponding extrusive and hypabyssal terms (rhyolites, porphyries). Leucogranites are the most important resources among granitoids, even though half of all mining operations in the World reside on pegmatites. A few alkaline complexes with silica-undersaturated rocks are supplying the ceramic industry: both nepheline syenite and nepheline phonolite (and related intrusive and extrusive lithotypes). Intermediate igneous rocks (syenite, trachyte) are seldom exploited as fluxes, but the recourse to basic terms (gabbro, anorthosite, basalt, andesite, etc) is common in red firing products. Fluxes of sedimentary origin are obtained from feldspathic arenites, mainly arkoses. Metamorphic and metasomatic rocks are extensively utilized by the ceramic industry, especially albitites (the most important source for the ceramic tile industry) and phyllites. Deposits generated through low temperature hydrothermal (epithermal) alteration provide a set of peculiar fluxes (e.g., eurite and pottery stone) characterized by a significant amount of low melting minerals, such as sericite. Skarn deposits are the main source of non-feldspathic fluxes, represented by ores rich in talc, wollastonite, chlorite, diopside. The compositional variability in the deposits of each source is represented through diagrams accounting for the relevant parameters for the ceramic industry: equivalent amount of feldspars, Na/K (or Ca/Mg) ratio, and concentration of chromophores (Fe<sub>2</sub>O<sub>2</sub> + TiO<sub>2</sub>). Such a global view is intended to foster studies on flux deposits, focusing on crucial aspects for the ceramic raw materals industry, like the existence of geological constraints to the occurrence of given ore types, or the definition of a genetic model for strategic resources, like albitite deposits.

Dondi, M. (2018): Feldspathic fluxes for ceramics: Sources, production trends and technological value. Resources, Conservation and Recycling, 133, 191-205.

## A complete approach for artificial ageing and decay analysis on some types of carbonate stones from Apulia (southeastern Italy)

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Keywords: Carbonate stone, decay, ageing test.

This study aims to perform an exhaustive method for producing artificial decay and analysing its effects on some types of Apulian carbonate stones, used as building and decorative material. In particular, it provides adequate experimental procedures and details for performing accelerated ageing tests and suitable techniques for investigating decay effects on the stone materials. In order to testify the approach proposed, five types of Apulian stones were chosen, different in terms of fabric and strength: a very compact calcilutite from Apricena and Trani basins, a porous calcilutite from Trani, a porous calcisiltite from Carovigno, a dolostone from Poggiorsini and a calcarenite from the Cursi-Melpignano quarry district.

For each group of the stones, selected samples were treated using several experimental artificial ageing tests, considering the environmental conditions in which these materials are locally placed on building structures. The ageing consisted of treatments to high temperature and thermal shocks, exposure to saline solutions and SO<sub>2</sub> atmosphere. Before, during and after ageing tests, elaborated methodology was applied to check and measure changes on the stones, in terms of chemical and mineralogical composition and physical properties. To this aim, several analytical techniques and methods were applied, such as X-ray diffraction and fluorescence, scanning electron microscopy, mercury intrusion porosimetry, ultrasound propagation velocity measurement. Description of the induced decay and relationships with natural processes were also presented. A different behaviour of the stone types was observed for each ageing test, mainly linked to their fabric, porosity and strength. Experimental conditions and procedure for performing ageing tests were defined and their efficiency in reproduction of deterioration environments was validated.

## Electrochemical atomic layer deposition to grow a p-n junction with binary sulphides

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Keywords: Electrochemistry, Sulphides, Energy.

Thin-film solar cells are the ones that show better performances (higher durability and conversion efficiency), among the technologies alternative to silicon-based devices. Their main drawback is the production process, which is today limited by the need of rare and expensive elements (the common thin film cells use CdTe or Cu(In,Ga)Se<sub>2</sub>). Additionally, the processes for their fabrication are usually energy expensive. Therefore the research in this field focus: 1) on the materials, to the aim of minimizing the exploitation rare elements and 2) on more sustainable production processes. Compounds such as Kesterites (CZTS, ternary and quaternary copper and zinc sulfides) could be used in virtue of their semiconductor behavior. Moreover, to simplify the productive process, electrodeposition from acqueous media was proposed. In this context, E-ALD (Electrochemical Atomic Layer Deposition) method seems a legit alternative to the high pressure and temperature methods used since today. This work focused on the characterization of the structure of two layers of semiconductors, deposited by means of E-ALD one above the other. We performed a thorough electrochemical characterization of these compounds resulting in a reproducible setup to deposit these junctions. Moreover, sulphides single compounds and their deposition by means of E-ALD method were largely characterized by means of Surface X-Ray Diffraction (SXRD) by our research group but their union to form a junction wasn't observed already. Recently, we focus on three different composite thin-films Cu<sub>2</sub>S/CdS/Ag(111), Cu<sub>2</sub>Zn<sub>2</sub>S/CdS/Ag(111) and CdS/Cu<sub>2</sub>S/Ag(111). In this communication we present a structural study of these composite ultra-thin films by means of electrochemical operando SXRD experiment performed at ID03 in Grenoble. We report reciprocal space maps of the samples with a structural interpretation of the main feature of the crystals and a comparison with the related compounds (CuZnS and Cu<sub>2</sub>S).

## Acid Mine Drainage and PTE distribution in a volcanic sulfur mine: the Thiorichia Mine, Milos Island, Greece

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Keywords: sulfur mine, Acid Mine Drainage, Mercury.

Acid Mine Drainage is a major environmental concern in sulfur-rich ore deposits and is widely studied in different geological contexts and for a variety of sulfide ore deposits. Milos volcanic sulfur mine represents in this picture a type of ore deposit whose acid mine drainage concern is little studied.

Milos Island is an active volcano of the Hellenic volcanic arc, with a main caldera collapse structure and a widespread secondary activity. The island hosts seven active mines that exploit bentonite (with the biggest mine in Europe), perlite and pozzolan deposits and several abandoned sulfur, kaolin, barite and manganese mines. Such intense mining activity in a 160 km<sup>2</sup> highly touristic island increases the importance of environmental studies for the sustainability of the island economy.

Sulfur mining at Milos started in V century BC, but the first modern mining concession dates back to 1862 and led to the opening of the Thiorichia Mine on the Eastern shore of the island. The mining site comprised several tunnels, sulfur purification facilities and other buildings for workers accommodation and administration. Sulfur purification was gained firstly with the Calcaroni method and later with Gill four chambers furnace. Extraction declined in the second half of last century and the mine was definitely closed in 1981.

During the field survey three different earthen materials were sampled: sands from the adjacent beach, stream sediments downstream from the purification plant and dumped material, close to the purification plant and uphill on the road leading to the mine. Beach samples are coarser (sandy gravels) due to wave erosion while both sediments and wastes fall in the range of sands and gravely sands.

Acid Mine Drainage potential was assessed with ABA procedure and results show that beach sands have no acid potential due to complete leaching of sulfur while sediments and wastes have variable acid potential closely related to the degree of sulfur oxidation.

Whole rock ICP analyses show that the highest environmental hazard for PTE is related to the high mercury content of stream sediments and wastes.

XRD-powder diffraction analyses show that quartz represents the overwhelming mineral phase in all the samples analysed. Minor phases as alunite-like minerals, micas, elemental sulfur, opal and kaolinite-like minerals have also been detected. The present work shows that Acid Mine drainage and PTE concern studies in sulfur deposits are particularly difficult due to the complete decoupling between the acid potential production, strictly related to the elemental sulfur content of the materials, and the potential release of PTE in the environment, probably associated to secondary clay and alunite-like minerals.

## ZSM-5 and L zeolites structural characterization after l-lysine amino acid adsorption

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Keywords: Zeolites adsorption, l-lysine amino acid, X-ray powder diffraction.

The current increase of amino acids production, driven by a synthesis improvement based on microbiological fermentation and chemical or enzymatic processes, demands for probing new sorption media suitable in amino acids separation methods. Indeed, the new challenge is to decrease the amino acids losses that occur during the several adsorption/desorption cycles. Among all the sorbents tested in amino acids sorption (e.g., activated carbons and minerals), synthetic zeolites represent an advantageous class of microporous materials due to their size and shape selectivity, resistance to swelling and thermal stability (Krohn et al., 2005). Although the efficiency of hydrophobic zeolites has been already proved (Munsch et al., 2001), no crystallographic information on the location of those extraframework molecules within the zeolite channels are available. In this contribution, new crystallographic results on two samples of ZSM-5 (MFI topology, Si/Al ratio 21 and 51, respectively) and one sample of L (LTL topology, Si/Al ratio 61) zeolites after adsorption of l-lysine are reported. The sorption process of as-synthesized ZSM-5 and L samples was carried out by means of the batch method (pH=5.5). After contact, kinetics and adsorption isotherms were collected through Capillary Electrophoresis separation technique. X-ray powder diffraction patterns of loaded samples were collected through synchrotron radiation at the MCX Beamline (Elettra, Trieste) at Room Temperature ( $\lambda = 0.8270$  Å, and  $2\theta$  range = 1-65°). Rietveld structural refinements (carried out in the monoclinic and hexagonal symmetry for ZSM-5 and L zeolite, respectively), and processed through the GSAS-EXPGUI software package, highlight on the presence of l-lysine extraframework molecules within zeolite channels (testify through difference Fourier maps analysis). In good agreement with thermal analysis, it results that the pore structure (1-dimensional channel) of L zeolite favours the adsorption of l-lysine. Among ZSM-5 samples, higher volumes of l-lysine compound were detected in SAR 21, thus confirming that the higher the SAR the lower the sorption capacity. These data on ZSM-5 are also corroborated by the comparison of the unit-cell parameters: the higher the 1-lysine content the lower the lattice parameter values. This multidisciplinary study allowed to characterize the sorbent structure after l-lysine adsorption and probed the interaction between the sorbent medium and the amino acid molecule. All the information gained suggest that both sorbents tested are particularly performing, albeit L zeolite is more efficient when applied in l-lysine adsorption processes.

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#### The use of surface modified natural Zeolites (SMNZs) as ibuprofen carriers

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Keywords: SMNZs, surfactant, ibuprofen.

In the last years, several studies dealt with the use of the natural zeolite-rich rocks as carriers in the loading and *in vitro* release of Ibuprofen (Mercurio et al. 2018 and references therein). The adsorption of these drug molecules is generally improved by external surface functionalization of zeolite, by interaction with specific cationic surfactants replacing the native cations. The obtained composite has been called Surface Modified Natural Zeolite (SMNZ).

In this frame, selected starting materials have been characterized from mineralogical and technological point of views by means of several analytical techniques and methods (Cappelletti et al., 2017). Moreover, an operative protocol for a fast functionalization of zeolite-rich rocks applicable at industrial scale were also provided (de Gennaro et al. 2016). In order to improve the knowledge of ibuprofen-SMNZ composite materials, loading and release performances were determined by means of equilibrium isotherms as well as loading and release kinetic runs. Whereas experimental data were fitted using a non-linear regression. Results suggested that NSAIDs sorption mechanisms occurring in SMNZs were due to the simultaneous occurrence of external anionic exchange process (predominant) and subordinately partition into the hydrophobic portion of micelle.

Influence of partition is strictly related to the formation of a complete or patchy bilayer onto the surface of zeolite support, as well as to the type of drug as a function of its hydrophobicity and molecular conformation.

A fast Ibuprofen loading was recorded for the SMNZs achieving its maximum according to: i) the type of zeolite (and zeolite contents) and the type of surfactant and ii) the anion exchange capacities (AECs) of examined SMNZs. Recent research evidenced a prompt Ibuprofen release within the first 30-50 min, making these natural materials suitable to provide rapid soothing effects. For a more sustained drug release, pharmaceutical form and experimental conditions must be properly considered.

These studies lead several implications concerning the intended use of natural zeolite-rich deposits, emphasizing the role of the geologists in the characterization of raw mineral materials for high-value technological applications.

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## Arsenic removal from contaminated water: environmental application of Maghemite nanoparticles - preliminary results

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Keywords: Maghemite nanoparticles, Arsenic, Water remediation.

Among toxic metals, Arsenic (As) is a Class A carcinogen. It is naturally present in water in different oxidation states: predominant are the trivalent form (As<sup>III</sup>), as  $H_3AsO_3$  at pH < 9, and the pentavalent form (As<sup>V</sup>) as oxyanion at neutral pH ( $H_2AsO_4^-$  and  $HAsO_4^{-2}$ ).

The main sources of As pollution are industrial processes (i.e. glass industry, wood treatment and agrochemicals) even though naturally occurring high concentrations have been documented in alluvial groundwater (Carraro et al., 2015). World Health Organization (WHO) fixed the threshold limit in drinking water at 10  $\mu$ g l<sup>-1</sup>(WHO, 2017).

Many methods are currently used for removing As from drinking water, such as chemical precipitation, adsorption and anion exchange, even if they present drawbacks in term of sludge generation and high operational costs; in this field, nanoparticles are emerging as one of the most promising new technique for soil and water remediation.

In this work, a maghemite nanoparticle, called SAMN (Surface Active Maghemite Nanoparticle), is applied for the removal of both As<sup>III</sup> and As<sup>V</sup>. It is a superparamagnetic nanoparticle constituted of maghemite characterised by specific surface chemical behaviour, without any coating or superficial modification, high surface area-to-volume ratio, low toxicity, strong absorption ability and stability in water for months as colloidal suspension (Magro et al., 2016).

The removal efficiency of  $As^{v}$  by SAMNs was tested in laboratory solutions, under variable testing conditions, such as pollutant concentrations, temperature and pH of the solution. Experiments evidenced that SAMNs are able to remediate water at high concentrations of  $As^{v}$  (~5.6 mg/L) with an important pH dependence, and 99 %  $As^{v}$  was removed at pH 3.0, while this amount decreased to about 70% at pH 9.0. Kinetic investigations showed an initial fast rate of  $As^{v}$  adsorption from the aqueous solution (~50%) within the first 5 minutes, followed by a slower uptake reaction.

Further experiments are in progress to validate the efficiency of SAMNs also for the removal of As<sup>III</sup>.

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## Nonsulfide mineralization in the Gorno Zn prospect (Bergamo, Italy): new data on the Oltre il Colle-Pian Bracca exploration area

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Keywords: Zn-Pb ore deposit, Zn nonsulfide minerals, Gorno Zn prospect.

The Gorno Zn-Pb(Ag) deposit, located in the Bergamo province (northern Italy), is a Mississippi Valleytype (MVT) mineralization belonging to the "metallogenic province" of the eastern Alps. Several other MVT deposits are comprised in this region, including the former Bleiberg, Raibl and Mežica mines. The Alpine district has a long history of mining, extending back to pre-Roman times. The Gorno mine was active since the beginning of the 20<sup>th</sup>century and ceased operations in the early 1980s, even though excellent intercepts of zinc, lead and silver had been identified in numerous locations, including the so-called "Colonna Zorzone" area (ready to be developed) before operations prematurely stopped. Extensive drilling carried out from 2015 onward by Alta Zinc Ltd. (the current owner of mining concession and exploration licenses in the area) allowed to estimate in the Colonna Zorzone at least 3.3 Mt JORC compliant indicated+inferred resources at 4.9% Zn, 1.3% Pb, and 27.2 ppm Ag (cut-off grade of 1% Zn). In this area, the mineralization, consisting of sfalerite and galena (with inclusions of Ag-bearing sulfosalts), is hosted in Triassic carbonaceous schists of the Calcare Metallifero Bergamasco Formation, and has mostly a stratabound orientation, with an overall thickness ranging from 6 to 14 m.

The presence of an oxidized (nonsulfide) Zn-Pb mineralization has been identified in a further mineralized nucleus located in the Oltre il Colle-Pian Bracca area, in a partially developed network of galleries extending 500 m below the surface, between 990 to 1028 m.a.s.l. This high-grade nonsulfide mineralization, hosted in the Triassic limestones of the Breno Formation underlying the sulfide-bearing schists, occurs in sub-vertical breccia bodies associated with several normal faults that displace the sulfide lenses. The nonsulfide concentrations commonly show Zn grades around 20 wt.% (locally higher than 35 wt.%) and a mineral association mostly consisting of smithsonite, hydrozincite, hemimorphite, cerussite and anglesite. These minerals formed after the alteration of pre-existing sulfides, when Zn and Pb precipitated in the fracture network of the fault zones, after the reaction of the Zn-Pb-bearing fluids with the carbonate host rock.

The oxidized Zn-Pb bodies occur in an area of the Gorno Zn project, which is currently under exploration. Due to their high grades and low-cost metallurgy, if drilling operation will confirm their extension, the nonsulfide zones could further enhance the value of the Gorno deposit, as well as the italian potential of metallic resources.

## Vitrification of Construction and Demolition Waste (CDW): prospects for new green building materials

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Keywords: CD-Waste, recycle, vitrification.

Construction and Demolition Waste materials are normally produced during new constructions and restorations, but they also include the rubble unfortunately produced by catastrophic events like earthquakes. The amount of waste in the construction sector is continuously growing and a major European challenge is to ensure by 2020 that at least 70% of Construction and Demolition Waste (CDW) is intended for reuse and recycle. All EU members will have therefore to implement waste management practices needed to meet this Community target.

The major problem with recycling of CDW is that it is highly heterogeneous, depending on the construction locations and building styles: concrete, rocks, bricks, sanitary ware, ceramic tiles, roof tiles, plaster, wood, glass, metals, plastic, as well as hazardous waste like asbestos. Currently, in Italy, 75 % of CDW is being recycled, roughly twice the average percentage among the EU members (many of whom lack confidence in the composition and quality of CDW-based products).

The vitrification of CDW may represent a useful technique to increase significantly the reuse of this material, which currently is still largely limited to use as a low-grade filling aggregate. Here we report the results obtained from a series of thermal treatments carried out in air at different temperatures and durations (1000-1250°C and 2-16 hours). The aim is to study the CDW vitrification process to determine the best conditions useful to obtain a glass-ceramic material and investigate its characteristics for potential applications. The samples were analyzed for mineralogical composition by powder X-Ray Diffraction (XRD) after each thermal treatment, observed under the optical microscope and analyzed by Scanning Electron Microscope (SEM).

The samples produced at high temperature are quite homogenous in composition, glassy with no significant amounts of crystalline compounds, except for the presence of gehlenite. SEM analysis also revealed that the main components after melting are  $SiO_2$ ,  $Al_2O_3$ , CaO. The parameters to be determined are the influence of the CDW mineralogical/chemical composition on the glass composition and the minumum time and temperature necessary to achieve vitrification as a function of composition. Although the high-temperature melting is an energy-consuming process emitting also variable amounts of  $CO_2$ , the Life Cycle Assessment of a final product to be used as tile suggest that the GWP (Global Warming Potential) would be lower than values for ceramic tiles and cement-based terrazzo-tiles. In fact, a tile produced with this process would be saving 100% of raw materials and contain no cement, in fulfillment with the requirements introduced by the CAM (Criteri Ambientali Minimi) and GPP (Green Public Procurement) for the construction sector, as well as following the EU directive on waste and landfills.

## The Wingellina Ni-Co laterite deposit (Western Australia): mineralogical association in an atypical oxide-type laterite

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Keywords: Ni-Co-Laterite, Mesoproterozoic, Australia.

The Wingellina Ni-Co laterite project (Western Australia), which belongs to the Company Metals X, comprehends a Probable Mining Reserve of 168 Mt of limonitic ore, grading at 0.98% Ni and 0.08% Co. The laterite profile, developed from the weathering of the mafic to ultramafic layered intrusion of the Giles Suite (Mesoproterozoic), is lithologically heterogeneous and consists of two main zones: a Fe- and Mn-(hydr)oxides rich limonite and a phyllosilicates-rich saprolite.

The exploitable reserves occur within the limonite unit, where Ni- and Co-bearing goethite and hematite are ubiquitous. Nevertheless, the highest-grade zones of the limonitic mineralization are chiefly associated with the occurrence of MnO-rich layers. The lithiophorite-asbolane intermediate is the most widespread Mn-hydroxide, where the higher Ni- and Co grades occur. Other ore-bearing Mn-hydroxides are romanèchite, ernienickelite-jianshuiite, manganite, and k-birnessite. The chemistry and the textural association between the lithiophorite-asbolane and the other Mn-hydroxides suggest that the main trigger of the Ni- and Co-enrichment in these phases was the leaching of alkali and alkaline earth elements (such as K and Ba) and the subsequent capture of transition metals, including Ni, Co<sup>3+</sup>, Al and Fe<sup>3+</sup>(Putzolu et al., 2018).

In the Wingellina laterite, even if it is formallyclassified as an oxide-type deposit, also the silicate-bearing part of the profile (i.e. the saprolite zone) has a remarkable Ni-grade (Putzolu et al., in press): this being evidence that the current classification model for Ni-laterites has to be used with care. Preliminary mineralogical and chemical studies performed on the silicate zone showed a certain degree of heterogeneity of the mineralogical association, which likely depends on the nature and the degree of serpentinization of the protolith. In particular, when the laterite profile is formed from the unserpentinized gabbro units, the saprolite zone consists totally of Ni-rich smectites. On the contrary, the weathering of serpentinized peridotites gives rise to the formation of Mg(Ni)-silicates (lizardite and talc) in the lower saprolite zone, which are subsequently replaced by Ni-smectites.

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## Phillipsite and Al-tobermorite from Surtsey - Alteration in Basaltic Tuff and Analogies with Ancient Roman Concrete

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Keywords: Phillipsite, Al-tobermorite, Surtsey.

Studies of ancient Roman marine concrete drill cores show that an unusual, calcium-silicate-hydrate mineral with cation-exchange properties, Al-tobermorite  $\{[Ca_4(Si_{5.5}Al_{0.5}O_{17}H_2)]Ca_{0.2}Na_{0.1} \cdot 4H_2O\}$ , crystallizes in relict lime clasts and in diverse components, pumice clasts, dissolved feldspar, and relict voids, of the mortar fabric (Jackson et al, 2017). The crystallization of Al-tobermorite, in association with other authigenic mineral assemblages, apparently records the response the concrete to subaerial and submarine fluid interactions over 2000 years.

In Roman marine concretes, lime mortars produced with weakly or not zeolitized Campi Flegrei *pozzolana* and seawater created a highly alkaline, but relatively short-lived pozzolanic system buffered by calcium hydroxide, which produced C-A-S-H cementing binder and Al-tobermorite at <95 °C (Jackson et al, 2017). Post-pozzolanic Al-tobermorite and zeolite crystallization occurred at lower temperatures, in association with clasts of Campi Flegrei Neapolitan Yellow Tuff and *pozzolana* (de Gennaro et al., 2000). The *in situ* phillipsite reacted to produce additional Al-tobermorite at ambient seawater temperatures. In subaerial mortars, carbonation of Campi Flegrei zeolite within pumice apparently released alkaline earth elements, and also produced Al-tobermorite (Jackson et al, 2017).

In nature, Al-tobermorite crystallization is commonly related to hydrothermal alteration of basalts. Altered basaltic tuff in 2017 drill cores from Surtsey volcano, a 50-year-old oceanic island in Iceland, have been investigated at DiSTAR (Federico II University, Napoli, Italy) within the SUSTAIN (Surtsey Underwater volcanic System for Thermophiles, Alteration processes and INnovative Concretes) project, sponsored by the International Continental Drilling Program. The hydrothermal system of Surtsey was dominated by steam vapor above sea level and by a submarine hydrothermal zone in 1980 (Jakobsson & Moore, 1986); substantial cooling has now occurred above and below sea level. During alteration, glass shards in tephra were chemically altered and hydrated, and crystallization of Al-tobermorite with various zeolites occurred as mineral cements in voids. These are similar to processes in ancient Roman marine concretes (Jackson et al, 2017).

Further investigations of Al-tobermorite in geological environments will be important to in clarifying differences with analogous crystals in Roman concretes. In both environments, the crystals act as mineral cements that reinforce cohesion and potentially enhance fracture toughness.

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## Evolution of Mineral and Melt Composition during Reactive Sintering of Porcelain Stoneware Bodies

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Keywords: Porcelain stoneware, Reactive Sintering, vitrification.

Porcelain stoneware is sintered by partial vitrification, through viscous flow of an abundant liquid phase formed at high temperature. Such a process must be kept under strict control to achieve the desired properties of final products and prevent defects induced by pyroplasticity. The present contribution will overview the evolution of phase composition of porcelain stoneware during firing at different temperatures and soaking times. Seven ceramic bodies (mainly sodic or potassic and mixed Na-K) consisting of a mixture of ball clay, quartz and feldspars, were taken into account. The firing behavior was studied with ex-situ measurements (after heating treatment in roller or chamber furnaces) and *in-situ* (using a hot stage microscope). The firings were conducted in two distinct ways: dynamic (*i.e.* with a ramp simulating the industrial heating cycle in a roller oven) and static, by inserting the sample into the chamber furnace directly at the maximum temperature and permanence for increasing times, interrupted by a quenching in cold water. Each mixture was characterized from the chemical point of view and, once fired, its phase composition was determined by quantitative XRPD (Rietveld method). The transformations affecting the minerals of the starting mixture determine a continuous variation of the phase composition during the heating treatment: industrial firing schedules let feldspars to melt quickly (K-feldspar>plagioclase) - largely melted at 1100°C, completing their dissolution in the liquid phase before 1200°C - while quartz is only partially dissolved at the highest temperature. These variations involve the liquid phase, already abundant around 1100°C, which changes its chemical composition according to the dynamic equilibrium established with both the residual minerals (quartz, feldspar) and the new crystalline phases formed during the firing (mullite). Once formed, mullite is gradually dissolved, though by a decreasing rate, making the melt increasingly peraluminous. Variations of the chemical composition of the liquid phase reflected on its physical properties, particularly on viscosity and surface tension, which define the densification kinetics in the sintering process. It has been observed that the melt viscosity lowers rapidly up to 1200°C, but tends to increase slowly during soaking. All the physical and mineralogical features studied affect the sintering kinetics and pyroplasticity. This latter depends on both the melt viscosity and the amount of crystals suspended in the liquid phase. In fact, firing deformation could scale with crystals shape and size distribution, which in turn reflect in a complex way the dissolution rate of mullite and quartz into the melt (buffered by silica oversaturation and strong peraluminous character).

# Session S25 Puzzle crystallography of inorganic structures. A tribute to Fiorenzo Mazzi

Conveners AND CHAIRPERSONS Roberta Oberti (IGG-CNR, Pavia) Maria Chiara Domeneghetti (Università di Pavia)

## Site distribution of Mn<sup>2+</sup> and Mn<sup>3+</sup> and structural formula of minerals in the axinite-(Mn)-tinzenite series

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Keywords: axinite, tinzenite, crystal chemistry.

Fifteen samples of axinite from Liguria (Italy) were investigated by a multi-analytical approach (EMPA, SREF, UV-VIS-NIR) with the aim to determine compositional relationships, intracrystalline cation distribution and site preference along the axinite-(Mn)-tinzenite series.

The structural formula for triclinic (Space Group *P*-*1*) axinite mineral-group was proposed by Andreozzi et al. (2004):  ${}^{VI}[X1X2YZ1Z2]_{2}{}^{IV}[T1T2T3T4T5]_{2}O_{30}(O_{w}OH_{1-w})_{2}$ , where VI and IV are coordination numbers; *X*1 = Ca and very minor Na; *X*2 = Ca (in axinite) or Mn<sup>2+</sup> (in tinzenite); *Y* = Mn<sup>2+</sup> [in tinzenite and axinite-(Mn)], Fe<sup>2+</sup> [in axinite-(Fe)] or Mg [in axinite-(Mg)], with minor Al and Fe<sup>3+</sup>; *Z*1 = Al and minor Fe<sup>3+</sup>; *Z*2 = Al; *T*1, *T*2 and *T*3 = Si; *T*4 = Si (and very minor B); *T*5 = B and minor Si.

Very few studies are focused on minerals of the axinite-(Mn)-tinzenite series, and tinzenite content is chemically documented up to ~ 85-90% (Grew, 2018). Only three samples have been structurally studied so far, with tinzenite contents of 20% (Belokoneva et al., 1997), 58% (Belokoneva et al., 2001) and 72% (Basso et al., 1973). Namely, only the last two samples may be classified as tinzenite.

The samples from Liguria cover almost the entire series from zero to 82% tinzenite, and no compositional gaps are observed. Few samples show axinite-(Mn) core and tinzenite rim. Based on Ca and Mn contents, 7 samples can be classified as axinite-(Mn) and 8 as tinzenite. Crystal structure of the Mn-richest sample with tinzenite content of 82% was refined to an *R*1 index of about 2% using 3734 unique reflections collected with MoKa radiation. Structural, chemical and spectroscopic data were integrated, and accurate atomic site distribution in the tinzenite structure was obtained. For the first time, the presence of Mn<sup>3+</sup> up to 0.3 apfu is documented, with contents increasing towards tinzenite. The Mn<sup>3+</sup> does not substitute Mn<sup>2+</sup> at the *Y* site, but substitutes Fe<sup>3+</sup> and Al at Z1. Accordingly, the structural formula for minerals in the axinite-(Mn)–tinzenite series may be written as:  ${}^{X1}(Ca_2){}^{X2}(Ca_{2-x}Mn^{2+}_{2+x}){}^{Y}(Mn^{2+}){}^{Z1}_2(Al_{2-y}Mn^{3+}_{y}){}^{Z2}(Al){}_2[B_2Si_8O_{30}](OH)_2$ , with  $0 \le x \le 2$  and  $0 \le y \le 0.3$ .

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#### Beyond routine refinements in a routine way

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Keywords: Crystal structures, Refinement, Cation Ordering.

Structure refinement to the Bragg intensities obtained in a diffraction experiment provides a picture of the average structure of a material at the atomic scale. The life-long interest of Prof. Mazzi of the University of Pavia was to explore how to extract the true local structure of minerals from crystals which exhibit order/ disorder on different scales from stacking disorder in polytypes and twinned crystals, to atomic order/disorder. With the advent of modern diffractometers that provide precise and accurate intensity data very rapidly to high resolution, it is now possible to re-examine the validity of even the fundamental models that underlie the interpretation of that data in conventional refinements, and to solve old crystallographic puzzles in new ways.

We have collected high-resolution data on sub-100um size crystals of olivines with a commercial instrument, the Oxford Diffraction SuperNova diffractometer equipped with a Mo-target microsource, and a Pilatus 200K area detector. Conventional structure refinements of olivine with independent atom models confirm the general observation established by the Pavia school that the refined site occupancies are strongly dependent on data resolution. For olivines the site occupancies do not correspond to the true chemical composition. The reason is that the diffraction intensities contain the signal of the diffraction effects of the non-spherical electron distributions due to bonding in the crystal. The use of multipole refinement models or similar is precluded because their meaning is unclear in the context of mixed site occupancies as found in all crystals belonging to mineral solid solutions. Surprisingly, simplistic refinement models such as the electron-in-bond model provides correct compositions (and by inference correct site occupancies) for olivine independent of data resolution.

These tests show that modern structure refinements, properly performed, are not limited by the accuracy or precision of modern laboratory X-ray diffraction data which provide an unbiased map of the electron density of the crystal. The limitations of modern structure refinements are in the refinement models used to interpret the data. Thus, while bond lengths and angles are determined consistently by different models, site occupancy refinements in olivine are biased to the wrong results by the conventional independent atom model. This puzzle can be overcome by the careful choice of physically-meaningful but simple refinement models.

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## Rebulite and jankovicite: Tl<sub>5</sub>(As,Sb)<sub>13</sub>S<sub>22</sub> solid solution series and the puzzle of symmetry change

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Keywords: modular structures, As-Sb solid solution, Tl sulfosalts.

The realm of the crystal structures of sulfosalts (complex sulfides of Vb group semimetals with one or more metal or semimetal elements) is a complex one featuring a number of modular structures of diverse kinds. The sulfosalts of thallium are among the most complex ones with some exceptional "twists" in applications of modularity. Rebulite and jankovicite are both mixed As/Sb sulfosalts with the general stoichiometry  $Tl_5M_{13}S_{22}$ , where M stands for As+Sb. The compositional field of rebulite extends from around  $As_{10}Sb_3$  to around  $As_{7.5}Sb_{5.5}$  ratio, that of jankovicite from around  $As_{5.5}Sb_{7.5}$  to around  $As_3Sb_{10}$ , as determined by syntheses (Balic-Zunic et *al.* 2015). The crystal structures are built of structural slabs of unique complex structure and essentially the same topology in both crystals. The difference between the two crystal structures is in the overall crystal symmetry, which is  $P2_1/c$  in rebulite and P-I in jankovicite, caused by a difference in the structural slab twinning. The slabs in jankovicite are related by -1 operations over the slab boundaries, whereas it is the case for each other slab boundary in rebulite, the twinning on the other boundaries being through  $2_1$  operations. The reasons for seemingly unusual solid As/Sb solution (standard effective ionic radii of  $As^{3+}$  and  $Sb^{3+}$  are 0.58 and 0.76 Å, respectively) and for the change in symmetry over the compositional gap will be described in the presentation.

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## Crystal-chemistry of tetrahedrite group minerals from the Apuan Alps hydrothermal ores (Tuscany, Italy)

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Keywords: tetrahedrite group minerals, crystal chemistry, sulfosalts.

Tetrahedrite group minerals are a series of cubic sulfosalts having general formula  ${}^{M2}A_6{}^{M1}(B,C)_6{}^{M3}X_4{}^{S1}Y_{12}{}^{S2}Z$ , where  $A = Cu^+$ ,  $Ag^+$ ,  $B = Cu^+$ ,  $Ag^+$ ,  $C = Zn^{2+}$ ,  $Fe^{2+}$ ,  $Hg^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $X = Sb^{3+}$ ,  $As^{3+}$ ,  $Bi^{3+}$ ,  $Te^{4+}$ ,  $Y = S^{2-}$ ,  $Se^{2-}$ , and  $Z = S^{2-}$ ,  $Se^{2-}$ ,  $\Box$ . Owing to the potential occurrence of several iso- and heterovalent substitutions, the tetrahedrite group is likely the most complex isotypic series among sulfosalts (Moëlo et al., 20008). Moreover, the chemical variations in tetrahedrite group minerals could be able to reflect the evolution of physico-chemical parameters of ore fluids in hydrothermal systems (e.g., Wu & Petersen, 1977; Staude et al., 2010). Consequently, an accurate crystal-chemical characterization of these minerals could be interesting from both mineral systematics and ore geology.

Members of the tetrahedrite group are well-known in hydrothermal veins from the Apuan Alps metamorphic complex (Tuscany, Italy). The first descriptions were reported in (Kersten, 1843; Fiedler, 1846): and since then the occurrence of chemical variations was noted, in some cases leading to the proposal of new minerals (e.g., "coppite" and "frigidite" (Bechi, 1863; D'Achiardi, 1881). However, the only known modern data have been reported in (Carrozzini et al., 1991).

In the framework of a comprehensive study of sulfosalt assemblages from the hydrothermal ores of Apuan Alps, samples of tetrahedrite from different kinds of ore deposits have been investigated coupling single-crystal X-ray diffraction studies and chemical analyses. Data clearly indicate that the member of the tetrahedrite group occurring in the Apuan Alps ore deposits are characterized by Cu as A and B cations, with minor to moderate Ag substitution, and by different kinds of divalent C cations (Zn, Fe, and more rarely Hg). As regards the X cations, a continuous series between Sb-rich and As-rich compositions has been observed.

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## From crystals to quasicrystals in the Khatyrka meteorite: There's plenty of room in the middle

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Keywords: approximant, intermetallic alloys, quasicrystals.

The Khatyrka meteorite formed 4.5 billion years ago during the earliest stages of the solar system and contains evidence of a heterogeneous distribution of pressures and temperatures during impact shock, in which some portions of the meteorite reached at least 5-10 GPa and 1200-1500 °C. During a nano-mineralogical investigation of the Khatyrka meteoritic grains, we have found a new phase with composition  $Al_{34}Ni_9Fe_2$ . The new phase represents the first natural periodic approximant to a decagonal quasicrystal. "Periodic approximant" is an accepted technical term that means the solid has nearly the same composition and atomic arrangement as a decagonal quasicrystal but its atomic arrangement is distorted in such a way that it is actually crystalline with a symmetry that satisfies the laws of crystallography for periodic structures.

The new mineral crystallizes in the space group *Pnma* (R1 = 2.46% for 2360 observed reflections [ $Fo > 4\sigma(Fo)$  level] and 110 parameters). The structure can be described as a four-layer stacking along [010]. The two atomic layers at y = 0 and y = 1/2 are puckered while the others at y = 1/4 and y = 3/4 are flat. The most prominent structure motifs are pentagonal flat and elongated bipyramids (PBP) with (Ni,Fe) atoms at the vertices. The PBPs appear as large pentagons in the flat layers. The apical (Ni,Fe) atoms of the PBPs, pentagonally surrounded by Al atoms, form the vertices of a pseudo-hexagon tiling in the puckered layers. The same kind of building units (in different arrangements) was already observed for several approximants.

The new approximant described here has not yet been observed among the products of laboratory experiments. It was found that at about 940 °C the decagonal phase  $(Al_{71}Ni_{24}Fe_5)$  transforms to  $Al_{13}(Fe,Ni)_4$ ,  $Al_3(Fe,Ni)_2$  and the liquid phase, and between 800 and 850 °C to  $Al_{13}(Fe,Ni)_4$ ,  $Al_3(Fe,Ni)$  and  $Al_3(Fe,Ni)_2$ . Although  $Al_{13}(Fe,Ni)_4$  shows chemical similarities with the new discovered mineral, it crystallizes with the monoclinic  $Al_{13}Fe_4$  structure and corresponds to the recently described mineral hollisterite [ideal chemical formula  $Al_3Fe$ ]. Also, Ni dominates significantly over Fe in the new phase.

Hence, natural  $Al_{34}Ni_9Fe_2$  is a new compound among the previously known synthetic phases in the deeplystudied Al-Ni-Fe system. Furthermore, it represents the first crystal approximant found in nature. As is the case for the quasicrystalline phases described in Khatyrka, the new phase could have formed during a shock event experienced by the Khatyrka meteorite in outer space or by other processes during the formation of the early solar nebula. An open question remains: Does the new phase represent a new, unpredicted thermodynamic stable compound at high pressure or is its formation the result of a favorable kinetic pathway that exists under shock conditions? It was indeed recently demonstrated that shock conditions can generate previously unknown quasicrystals in both the Al-Cu-Fe and Al-Ni-Fe system.

#### Structural constraints on the tourmaline site populations

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Keywords: Tourmaline, crystal structure, crystal chemistry.

Minerals of the tourmaline supergroup are cyclosilicates with essential B. They are the most common and the earliest B minerals formed on Earth, occurring typically in granites and granitic pegmatites but also in sedimentary and metamorphic rocks (Grew et al., 2016). Tourmalines are stable in environments that extend from the crust surface to ultrahigh-pressure conditions (diamond stability field) prevailing in the upper mantle.

The general formula is written as:  $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ , with  ${}^{[9]}X = Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , [] (= vacancy);  ${}^{[6]}Y = Al^{3+}$ ,  $Cr^{3+}$ ,  $V^{3+}$ ,  $Fe^{2+/3+}$ ,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Li^+$ ,  $Ti^{4+}$ ;  ${}^{[6]}Z = Al^{3+}$ ,  $Cr^{3+}$ ,  $V^{3+}$ ,  $Fe^{2+/3+}$ ,  $Mg^{2+}$ ;  ${}^{[4]}T = Si^{4+}$ ,  $Al^{3+}$ ,  $B^{3+}$ ;  ${}^{[3]}B = B^{3+}$ ,  ${}^{[3]}V = (OH)^-$ ,  $O^{2-}$ ;  ${}^{[3]}W = (OH)^-$ ,  $F^-$ ,  $O^{2-}$  being the most common constituents. The tournaline structure is usually described in space-group R3m and may be regarded as a three-dimensional framework of octahedra  $ZO_6$  that encompass columns of structural "islands" made of  $XO_9$ ,  $YO_6$ ,  $BO_3$  and  $TO_4$  polyhedra. The overall structure is a result of short-range and long-range constraints depending on the charge and size of ions, respectively (Bosi, 2018).

On the basis of about 330 structure refinements of tourmalines, the plot of the mean bond distances  $\langle Z-O \rangle$  versus  $\langle Y-O \rangle$  displays the occurrence of a dimensional difference ( $\langle Y-O \rangle - \langle Z-O \rangle$ ) in the range between 0.00 Å and 0.15 Å. This limited mismatch in the dimensions between  $\langle Y-O \rangle$  and  $\langle Z-O \rangle$  shows the presence of a long-range structural constraint for tourmaline minerals: values outside the range 0.00-0.15 Å cannot be tolerated by the structure. The stability field  $\langle Z-O \rangle$  versus  $\langle Y-O \rangle$  also describes and predicts the effects of the tourmaline structural stability on its chemical variability. In this regard, Bosi & Lucchesi (2007) predicted that the end-member compositions of the oxy-free species dravite, schorl and tsilaisite should never occur, neither as natural samples nor as synthetic samples, because their structures should be unstable: *i.e.*, the distances  $\langle ^{Y}Mg-O \rangle$  (= 2.082 Å),  $\langle ^{Y}Fe^{2+}O \rangle$  (= 2.136 Å) and  $\langle ^{Y}Mn^{2+}O \rangle$  (= 2.169 Å) are too large with respect to  $\langle ^{Z}Al-O \rangle$  (1.907 Å). At present, empirical studies on dravitic and schorlitic compositions with (Mg,Fe<sup>2+</sup>)  $\sim$  3 apfu and unsuccessful attempts of tsilaisite synthesis with Mn<sup>2+</sup> = 3 apfu, corroborated by the occurrence of tsilaisitic root compositions up to Mn<sup>2+</sup> = 1.6 apfu, can show the effect of long-range structural constraint on tourmaline site populations.

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## Complexity made simple: some cases in mineral structures

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Keywords: complexity in minerals, arrojadite group minerals, cancrinite complex sequences.

In its original formulation, Pauling's 5<sup>th</sup> rule of parsimony (Pauling, 1929) says that "the number of different types of constituents in a crystal tends to be small". Hawthorne (2006) argues that there are many minerals with a large number of chemical constituents (e.g. amphibole-group minerals, tourmaline-group minerals) and that what the rule emphasizes is that the number of topochemically different environments in a structure tends to be small. Therefore, we should expect limited topochemical complexity in natural minerals. However, some mineral groups seem not to obey this parsimony principle. The mineral localities with the highest diversity of mineral species, including some very complex ones, are related to alkaline pegmatite rocks, which also host a large number of chemical species. These localities also provide among the most complex mineral structures (in terms of both chemistry and topologies) and it seems that there is not an evident limit to the number of complex minerals awaiting for discovering and description. As a matter of fact, alkaline environments produce among the best training examples for the skilled mineral crystallographer. Seidozerite-supergroup minerals (Sokolova & Cámara, 2017) are a very enlightening example. If we consider high chemical variety and bonding environments another group of minerals that represents a very good example is the arrojadite group. Its members have an astounding number of atom sites in the asymmetric unit. Cations show very different bonding environments ranging from 4-fold up to 8-fold coordination. In arrojadite, the complexity is further increased by a pseudosymmetry that makes the structure appear as centrosymmetric where it is not (Cámara et al. 2006). Nevertheless, the high number of chemical elements involved and structural complexity do not always go along. That is the case of polytypism. Cancrinite complex sequences are one among the best examples: their structures have been classified as among the top 20 more complex structures (Krivovichev, 2013). Yet their composition is quite simple. Solving such complex structures is very challenging, although their relative topologies can be explained easily.

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#### The low temperature transitions of bornite

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Keywords: bornite, low-temperature, synchrotron

Bornite is a widespread sulfide mineral with nominal composition  $Cu_sFeS_4$ , perfectly fitting the appealing characteristics of technologically relevant multinary sulphides for thermoelectric (TE) technology. In this field, bornite has a recent history of success due to its interesting properties, non-toxicity and earth-abundance of its constituting elements (Suekuni & Takabatake T., 2016; Qin et al., 2017). During the last 40 years, its structure was the subject of several investigations at different temperatures with no conclusive structural determination of its polymorphs (Morimoto, 1964; Putnis & Grace, 1976). Several works suggest a structural ordering of Fe(III) in two specific sites at room temperature and the confirmation of these observation requires further investigation. To this aim, we improved the quality of the available diffraction data and attempted a further structural determination at cryogenic temperature. Specifically, we investigated a bornite sample (Natural History Museum of the University of Florence, Catalogue n° 14975, collected at the Cu-sulphide ore of Montecatini, Northern Apennines, Italy) by means of high resolution synchrotron X-ray powder diffraction (XRD), pair distribution function (PDF) analysis and X-ray absorption spectroscopy (XAS) between 10 K and 275 K. The experimental data confirmed the *Pbca* space group and strongly support the preferred location of Fe in bornite at 275 K. Furthermore, we found that the unit cell volume decreases continuously with decreasing temperature before undergoing an abrupt contraction below ~65 K, where a 1<sup>st</sup> order Pbca  $\rightarrow$  Pca2, structural transition takes place. The analysis of the vibrational mode yielded the primary active mode breaking the *Pbca* symmetry towards  $Pca_2$ . The  $Pbca \rightarrow Pca_2$ , structural transition was further investigated by firstprinciples calculations at DFT-PBE level of theory. Starting from the optimized structure only three phonon mode frequencies have been found lower than 5.6 THz with a finite imaginary component of about 6 THz. These modes distort the structure from *Pbca* to *Pca2*, confirming the experimental findings.

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#### Anomalous birefringence in garnets from SW Sardinia

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Keywords: skarn, anistropic garnets, grossular.

The garnet supergroup includes 32 species, 30 of which are cubic, but in literature garnets with intermediate compositions which show anomalous birefringence are known.

Birefringent, euhedral, centimeter-sized garnet, commonly black but also dark-green or orange, has been found in few decameter-sized skarn lenses close to Villa San Pietro (SW Sardinia). These lenses are made up by a massive, fine-grained, black to greenish matrix, mainly consisting of garnet, epidote, amphibole, wollastonite, quartz, calcite and graphite.

In thin section garnets appear colorless or pale rose or green and not pleochroic; black garnets host graphite inclusions in the core, commonly arranged in a cross shape, whereas orange and green garnets are usually inclusion-free. In crossed polars all garnets are birefringent and clearly zoned. The core has high interference colors and is surrounded by two or three concentric rims with different optical features. The inner rim, when present, is thin and with second order interference colors. The medium rim, representing the major volume of the whole crystal, is characterized by low birefringence and a tartan-like extinction that resembles cross-hatched twinning of microcline. The outer rim is similar to the inner one for thickness and birefringence. The transition between the different zones is sharp and with parallel and well developed faces.

Powder XRD analyses, even if not decisive due to the similarity of the patterns of many garnet end-members, indicate for all analyzed crystals a mix of grossular, andradite and possible katoite.

Microanalyses performed by SEM show that chemical zonation exactly follows the optical zonation. From the core to the outer rim,  $Al_2O_3$  decreases from 20-21 wt.% to 1-2 wt.% and FeO<sub>tot</sub> increases from 3-5 wt.% to 25-27 wt.%. Within the iron-rich medium rim, as well as in the outer rim several micrometer-thick, concentric bands showing enrichment in  $Al_2O_3$  and depletion of FeO<sub>tot</sub> are commonly present. CaO and SiO<sub>2</sub> are constant in all layers (~33 wt.% and ~39 wt%, respectively), whereas MnO and MgO contents are negligible.

According to Shtukenberg et al. (2005) the possible mechanism leading to anisotropy in garnets is the loss of "long-range order" in the calcium series of garnet; Antao (2013) suggests that the birefringence is induced by the intergrowth and relative strain of two or more different cubic end-members, as andradite and grossular.

Further analyses such as HR-XRD, Rietveld refinement and chemical analyses that can measure the possible hydroxyl content are required in order to decipher the origin and the evolution of these garnets.

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Antao, S.M. (2013): Three cubic phases intergrown in a birefringent andradite-grossular garnet and their implications. Phys. Chem. Min., 40, 705-716.

## Adding complexity to the nomenclature of the garnet supergroup: discovery of the new member {Ca<sub>3</sub>} [Sb<sup>5+</sup>],(Fe<sup>3+</sup>,Fe<sup>2+</sup>)O<sub>1</sub>,

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Keywords: garnet supergroup, garnet-type structure, Sb-oxide.

Here we report the crystal-chemical features of a new oxide mineral belonging to the garnet supergroup. Preliminary chemical data, obtained by SEM-EDS, shows Ca, Sb, Fe, Zn and minor amounts of Sn. Raman spectra do not indicate the presence of a hydrogarnet component. By means of Mössbauer spectroscopy the dominance of tetrahedral Fe<sup>3+</sup> is clearly demonstrated. Finally, single-crystal X-ray diffraction data were collected and the structure was refined. The mineral is cubic ( $R_{int} = 2.71\%$ ), with the unit-cell parameter a = 12.6093(2) Å. At the last refinement stage, with anisotropic atomic displacement parameters for all atoms and without constraints, the residual value converged to R1 = 1.97% for 305 observed reflections [ $F_0 > 4\sigma(F_0)$ ] level] and 19 parameters (R1 = 2.86% for all 401 independent reflections).

Altogether, our results point to the ideal formula  $\{Ca_3\}[Sb^{5+}]_2(Fe^{3+}_2Fe^{2+})O_{12}$ . Minor amounts of Sn<sup>4+</sup> at the octahedral site (*Y*) and Zn at the tetrahedral site (*Z*), were assigned on the basis of the preference of these cations shown for toturite and yafsoanite, respectively. The tetrahedral site (*Z*) shows a mean metal-O distance [1.888(1) Å], which well accounts for the entry of about one third of divalent cations (Fe<sup>2+</sup> and Zn). The dominance of Sb<sup>5+</sup> at the octahedral site (*Y*) is in good agreement with the mean distance [1.990(1) Å], slightly larger than the pure 5+-O> distance quoted in the literature. Due to the very large volume of the tetrahedron, the *X* dodecahedron (which shares two edges with it), shows a mean distance (2.490 Å) much larger than that observed in, for example, andradite ( $Z = Si_{3;} = 2.425$  Å), or even in schorlomite ( $Z = SiFe^{3+}_{2}$ ; = 2.440 Å). For the same reason, its degree of distortion is very low [ $\Delta(X-O) = 0.144$  Å].

The garnet supergroup is divided into groups on the basis of the total charge of the cations at the tetrahedral Z site (Grew *et al.* 2013); thus the mineral presented here could in principle be accommodated in the henritermierite group (Z charge = 8). However, in the classification of the garnet supergroup, members of the same group share (*i*) the same general formula, (*ii*) the same symmetry, and (*iii*) include minerals belonging to the same chemical class. In contrast, the mineral studied here has different properties from those of the henritermierite group (i.e., henritermierite and holtstamite): *i*) the general formula is  $Ca_3R^{5+}_2(R^{3+}_2R^{2+})O_{12}$  instead of  $Ca_3R^{3+}_2(R^{4+}_2[\_])O_{12}$ ; *ii*) it is cubic, whereas henritermierite and holtstamite crystallize in the tetragonal system; *iii*) it is not a silicate. For the above reasons, is could be proposed to introduce a new group - provided that more minerals of this type are discovered - as the subdivision of a group into subgroups is strongly discouraged (Grew *et al.* 2013).

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#### Mg-rich sulfate assemblages from the Fornovolasco mine (Apuan Alps, Tuscany, Italy)

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Keywords: epsomite, wilcoxite, crystal structure.

The Fornovolasco mine is well-known for the occurrence of several well-crystallized sulfates (*e.g.*, Mauro *et al.*, 2018). Several sulfate assemblages have been identified in the old tunnels, leading to the description of more than 15 different sulfate species, among which the new mineral species volaschioite (Biagioni *et al.*, 2011). Whereas the most abundant species are represented by iron sulfates, in a restricted area of the upper level of the old mining complex, an interesting Mg-rich sulfate assemblage has been discovered. Epsomite, MgSO<sub>4</sub>·7H<sub>2</sub>O, and pickeringite, MgAl<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>·22H<sub>2</sub>O, are the most common species, whereas magnesiocopiapite, MgFe<sup>3+</sup><sub>4</sub>(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>·20H<sub>2</sub>O, and wilcoxite, MgAl(SO<sub>4</sub>)<sub>2</sub>F·17H<sub>2</sub>O, are definitely rare. These species were identified through X-ray powder diffraction and EDS chemical analyses. Moreover, epsomite and wilcoxite, occurring in well-formed crystals, were used for single-crystal X-ray diffraction studies, allowing the collection of high-quality crystal-chemical data.

Epsomite is widespread as colorless equant grains, having a vitreous luster, or as euhedral prismatic crystals, up to 1 mm long. It occurs also as thin white acicular crystals, up to more than 3 cm in length. Mg, S and Fe are the only elements with Z > 9 detected during EDS analysis. Epsomite crystallizes in space group  $P2_12_12_1$ , a 11.8664(3), b 12.0150(3), c 6.8598(2) Å, V 978.03(4) Å<sup>3</sup>. The crystal structure of epsomite has been refined down to  $R_1 = 0.022$  on the basis of 3418 reflections with  $F_0 > 4\sigma(F_0)$  and 176 refined parameters. It is formed by an isolated SO<sub>4</sub> tetrahedron, a Mg(H<sub>2</sub>O)<sub>6</sub> octahedron, with s.o.f. (Mg<sub>0.87</sub>Fe<sub>0.13</sub>), and an interstitial H<sub>2</sub>O group, giving the formula (Mg<sub>0.87</sub>Fe<sub>0.13</sub>)(H<sub>2</sub>O)<sub>6</sub>(SO<sub>4</sub>)·H<sub>2</sub>O.

Wilcoxite is a rare mineral species reported from only a few localities worldwide. In the Mg-rich sulfate assemblage from Fornovolasco, it occurs as colorless to whitish euhedral crystals showing a distinctly triclinic symmetry, in some cases showing rounded edges, and intimately associated with epsomite. Wilcoxite crystallizes in space group *P*bar1, *a* 6.6748(1), *b* 6.7729(1), *c* 14.9076(2) Å,  $\alpha$  79.604(6),  $\beta$  80.163(6),  $\gamma$  62.475(5)°, *V* 584.90(4) Å<sup>3</sup>. The crystal structure has been refined down to  $R_1 = 0.038$  on the basis of 3074 reflections with  $F_0 > 4\sigma(F_0)$  and 207 refined parameters. In agreement with Peterson & Joy (2013), the crystal structure of wilcoxite is formed by isolated SO<sub>4</sub> groups, Mg(H<sub>2</sub>O)<sub>6</sub> octahedra, Al(H<sub>2</sub>O)<sub>5</sub>F octahedra, and three interstitial H<sub>2</sub>O groups. On the basis of the results of the crystal structure refinement, the formula of wilcoxite could be written as (Mg<sub>0.98</sub>Fe<sub>0.02</sub>)Al(H<sub>2</sub>O)<sub>11</sub>F·6H<sub>2</sub>O.

The occurrence of this Mg-rich sulfate assemblage is likely related to the action of  $H_2SO_4$  formed through the alteration of pyrite on the dolomitic host-rocks, resulting in the crystallization of Mg sulfates and gypsum.

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Peterson, R.C. & Joy, B.R. (2013): Wilcoxite MgAl(SO<sub>4</sub>)<sub>2</sub>F·17H<sub>2</sub>O, from Rico, Colorado: occurrence and crystal structure. Can. Mineral., 51, 107-117.

## A new iron (III) phosphate-sulfate from Apuan Alps (Tuscany, Italy): a difficult puzzle solved through a multi-technique approach

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Keywords: new mineral, crystal structure, ferric iron.

During the investigation of the secondary mineral assemblages from the Tl-rich pyrite ore deposits of southern Apuan Alps (Tuscany, Italy), we encountered a phase having an X-ray powder diffraction pattern not corresponding to those of any known compound. Consequently, we decided to further investigate such a phase.

The mineral occurs as globular aggregates formed by pseudo-hexagonal tabular crystals, pinkish in color, up to 100  $\mu$ m in size, closely associated with gypsum and related to pyrite oxidation. Chemical data indicated the occurrence of Fe, P, and S as the only elements with Z > 9. The Fe:P:S atomic ratio is 4:3:1.

The single-crystal X-ray diffraction study showed that this compound is triclinic, space group *P*bar1, *a* 13.376(3), *b* 13.338(3), *c* 10.863(4) Å,  $\alpha$  92.80(2),  $\beta$  91.03(2),  $\gamma$  119.92(2)°, *V* 1675.7(9) Å<sup>3</sup>. The metrics indicate a pronounced pseudohexagonal symmetry, in agreement with crystal morphology. The precession images showed the occurrence of sharp spots in reciprocal lattice planes perpendicular to **c**<sup>\*</sup>, while reflections are diffuse along **c**<sup>\*</sup>, likely as a consequence of stacking disorder. Owing to the low diffraction quality of available crystals, only a partial structural model can be proposed, converging to a conventional *R* factor of 0.23.

The crystal structure is formed by {001} heteropolyhedral layers, having composition  $Fe_4(PO_4)_3\Phi_{11}$ ( $\Phi$  = undetermined anions). Iron is octahedrally coordinated and the average bond distances suggest its trivalent nature. On the basis of bond-valence balance considerations, the  $\Phi$  species are likely represented by 1 (OH) group and 10 H<sub>2</sub>O groups. The [SO<sub>4</sub>] tetrahedra (three oxygen atoms were not located yet) hang on both sides of the layer towards the interlayer space, which is occupied by a number of water molecules, giving rise to a complex hydrogen bond system which keep layers together. The actual position of water molecules is very hard to be detected, also because of likely stacking disorder between neighbour layers.

The 3+ oxidation state of Fe has been confirmed by Mössbauer spectroscopy, whereas the H<sub>2</sub>O content was confirmed through thermogravimetric analysis. The data indicate that the ideal formula of this compound is  $Fe^{3+}_{4}(PO_{4})_{3}(SO_{4})(OH) \cdot 18H_{2}O$ . This formula is very similar to the ideal formula of zýkaite,  $Fe^{3+}_{4}(AsO_{4})_{3}(SO_{4})$  (OH)  $\cdot 15H_{2}O$ , a mineral with unknown crystal structure (Cech *et al.*, 1978), with (PO\_{4}) replacing (AsO\_{4}) groups.

Although some uncertainties remain for the complete characterization of this compound, there is no doubt that the structural information, coupled with sound crystal-chemical arguments, plays a crucial role in the solution of this nice crystallographic puzzle. All the available data seems to undoubtedly indicate that we are a dealing with a possible new mineral species.

Cech, F., Praha, J. & Novak, F. (1978): Zýkaite, Fe<sup>3+</sup><sub>4</sub>(AsO<sub>4</sub>)<sub>3</sub>(SO<sub>4</sub>)(OH)·15H<sub>2</sub>O, a new mineral. N. Jb. Miner. Mh., 1978, 134-144.

## Session S26

# Zeolites and porous materials: Unravelling the relations between crystal-chemistry, stability, structure and properties

Conveners And Chairpersons Rossella Arletti (Università di Torino) Annalisa Martucci (Università di Ferrara)

## Ultrasonic vs hydrothermal method: different approaches to form zeolites. Influence of both methods on zeolites time-dependent stability

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Keywords: fly ash, zeolites, sonication.

Zeolites (aluminosilicate consisting of alkaline and alkaline-earth elements) can be synthesized by several waste materials and through various processes the most used of which is represented by hydrothermal method. However, because of the reducing incubation time, the application of ultrasound has also received considerable attention in the last few years. In this study, the efficiency of direct sonication method (US) *vs* conventional hydrothermal process (HY) in synthesizing zeolites from waste material (fly ash) using seawater was investigated with the aim to determine differences in the mechanisms controlling the formation of these minerals with both approaches.

The results indicate that fly ash was converted into zeolite by applying both US and HY water bath processes. However, the comparison between the two methods shows that the action of sonication energy is generally superior to hydrothermal heating method in accelerating the transformation reaction of faujasite and A-type zeolite into a more stable form represented by sodalite. This is explained suggesting two different mechanisms for the zeolite synthesis by ultrasonic and hydrothermal processes. These mechanisms have been identified in the direct fast zeolite precipitation and in the geopolymers formation with a following slower zeolite growth within the amorphous mass by using ultrasonic and hydrothermal methods, respectively (Belviso, 2018).

Moreover, the data display that the two approaches also affect the solid state stability of the synthetic products in a different way over the years. The results, in fact, show that the quick crystallization of the more stable sodalite by ultrasonic treatment ensures a great stability of this synthetic product. The slower mechanism of geopolymer transformation into crystalline phases by the two-step hydrothermal process, instead, is responsible for a slow but progressive transformation of metastable synthetic products, so that faujasite and A-type zeolite give way to sodalite (Belviso, 2018).

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#### High-pressure adsorption of methanol in synthetic MFI- zeolites

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Keywords: MFI-zeolites, high pressure, methanol adsorption.

In the recent years, a raising interest related to the *P*-induced intrusion of ions/molecules from the socalled "penetrating" P-transmitting fluids into the zeolitic structural cavities have been object of a number of experiments. The *P*-induced adsorption process is controlled by a number of factors, recently reviewed by Gatta et al. (2018), and is enhanced when the kinetic diameter of the *P*-transmitting fluid's molecules is smaller than the free diameter of the framework cavities. This property can be exploited in potentially relevant technological applications. MFI-synthetic zeolites are presently employed as catalyst in the production of olefins (fundamental building blocks in the production of plastics, rubbers, or polymers) starting from methanol. This process is one of the most prominent alternative way for producing olefins avoiding the use of oil derivatives (Stöcker, 1999; Olsbye et al., 2012). The recent literature is focused on investigations of small- and medium pore-type microporous/zeolitic catalysts suitable for the methanol conversion to hydrocarbons. On this basis, in this study we investigated, by means of *in situ* powder and single-crystal synchrotron X-ray diffraction, the *P*-induced intrusion of methanol in different samples of synthetic MFI-zeolites, characterized by different framework and extraframework compositions, using a diamond-anvil cell. Thanks to these experiments we were able to: (i) draw conclusions about the use of pressure as preferential way to induce a "cold" adsorption of methanol into the zeolite cavities (and therefore potentially increasing the efficiency of the methanol-to-olefins process); (ii) analyze the role of the framework's and extraframework's crystal-chemistry in the adsorption process; (iii) compare the magnitude of the methanol intrusion in single crystal with respect to powders.

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## Spring or bumper/shock absorber: how different electrolyte aqueous solutions, intruded at HP, change the Si-chabazite energetic behavior

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Keywords: Zeolite, High pressure, X-Ray Powder Diffraction.

Hydrophobic porous materials, as pure-silica zeolites, can be used for energy storage by means of highpressure (HP) intrusion of a non-wetting fluid (Tzanis et al., 2012). After pressure release, the system can display different behaviors as spring, shock-absorber or bumper, depending on structural parameters (*i.e.* pore size) and the nature of the intruded liquid (Arletti et al., 2016). For example, with water or 10M LiCl aqueous solution as non-wetting liquid, the "\*BEA-type zeosil-liquid" system, shows a bumper behaviour, whereas, increasing the concentration of the solution (15-20M LiCl), a shock-absorber behaviour is observed (Ryzhikov et al., 2014). These results suggest that analogous modifications can occur in similar systems and the interactions among intruded species and host material drive the behaviour of the systems. The case of pure Si-chabazite (Si-CHA) is here presented, and the intrusion/extrusion behaviours of 3 electrolytic aqueous solutions (NaCl, NaBr and CaCl<sub>2</sub>) are compared. Structural investigations during intrusion/extrusion cycles were performed by in situ X-ray powder diffraction to unravel the nature of the intruded species and their interactions with the zeolitic framework. During compression, the 3 systems display similar trends as far as cell parameters evolution is concerned. Specifically, penetration of comparable extra-framework volumes occurred at similar P values. Independently on the nature of the penetrating media, the following main steps were recognized: i) water intrusion; ii) water and ions intrusion (~0.26 GPa); iii) reaching of the maximum penetration of the extra-framework species. Upon P release, the 3 systems present different behaviors. Si-CHA intruded by NaCl and NaBr aqueous solutions does not recover the initial cell volume and retains the intruded extra-framework species. On the contrary, CHA intruded by CaCl<sub>2</sub> completely recovers the initial cell parameters and both ions and water molecules are released. This data has been structurally interpreted on the basis of the electrolyte/ zeolite interactions. Interestingly, the extrusion behavior results to be mainly determined by the interactions of the anion with CHA silanol defects.

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#### Degassing and phase transitions at high temperature in Melanophlogite (Type I Clathrate)

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Keywords: melanophlogite, degassing, phase transition.

Melanophlogite (MEP) is a rare tectosilicate with a clathrate structure, formed by a microporous framework of corner sharing SiO<sub>4</sub> tetrahedra and isolated cages between them, which can host guest gaseous molecules, such as CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S and N<sub>2</sub>, depending on geological setting of MEP occurrence sites. MEP chemical formula is 46SiO<sub>2</sub>•2M<sup>12</sup>•6M<sup>14</sup>, where M<sup>12</sup> and M<sup>14</sup> indicate the smaller pentagondodecahedral [5<sup>12</sup>] and the larger tetrakaidecahedral [5<sup>12</sup>6<sup>2</sup>] cavities respectively (Tribaudino et al., 2010; Momma, 2014).

In this work, the results of a multi-analytical study on the high temperature degassing behaviour of Italian MEP from Fortullino (Livorno) and Racalmuto (Agrigento) are reported.  $CO_2$  and  $H_2S$  with minor amounts of  $CH_4$  are peculiar guest gases for MEP from Fortullino and Racalmuto respectively.

HT-XRPD (High Temperature X-Ray Powder Diffraction) on MEP from Fortullino has shown a phase transition at about 60 °C, as previously reported (Liu et al., 1997; Nakagawa et al., 2005), also revealed with DSC (Differential Scanning Calorimetry) on MEP from Fortullino and Racalmuto, denoting a second order transition between high temperature cubic structure and room temperature lower symmetry one.

TGA (Thermal Gravimetric Analysis) has shown similar profiles for MEP from Fortullino and Racalmuto, although the weight loss is lower in sample from Racalmuto than in one from Fortullino (4.4 wt.% vs 11.7 wt.%), due to partial occupancy of H<sub>2</sub>S, which has a lighter mass than CO<sub>2</sub>.

The onset of degassing is at about 200 °C, with no differences between two localities. At high temperature, MEP reacts to become cristobalite or quartz and, once degassed, has a very low short range order. Degassing reduces MEP structural stability, since guest gases act as template agent. Consequently, in a sedimentary area, MEP indicates local temperatures always lower than 200 °C, since, for higher ones, degassing and transformation of MEP in high temperature silica polymorphs are promoted. Moreover, since degassing causes the collapse of mineral structure and required synthesis temperatures are between 160 and 200 °C (Gunawardane et al., 1987), MEP can be considered as a marker for bracketing temperatures of fluids circulating during mineral formation.

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#### Syntheses of Melanophlogite (Type I Clathrate)

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Keywords: melanophlogite, syntheses, x-ray diffraction.

Melanophlogite (MEP) is a tectosilicate belonging to SiO<sub>2</sub> type I clathrate compounds, zeolite-like materials with microporous framework of corner sharing SiO<sub>4</sub> tetrahedra and pentagondodecahedral [5<sup>12</sup>] and tetrakaidecahedral [5<sup>12</sup>6<sup>2</sup>] isolated cages between them. MEP chemical formula is  $46SiO_2 \cdot 2M^{12} \cdot 6M^{14}$ , where M<sup>12</sup> and M<sup>14</sup> denote the smaller pentagondodecahedral and the larger tetrakaidecahedral cavities respectively. CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S and N<sub>2</sub> are guest gases in the voids (Tribaudino et al., 2010; Momma, 2014).

MEP is a rare mineral related to low temperature hydrothermal processes in connection with the gaseous activity (Tribaudino et al., 2008), so that a critical issue is MEP synthesis. MEP is potentially interesting for gas storage aimed at energy and environmental applications: an important target is to understand natural and synthesized MEP sorption and desorption processes.

We have synthesized MEP in quantities of hundreds of milligrams (likely for the first time, since there are no references) thanks to an optimized hydrothermal syntheses procedure. The actualization of syntheses has been proved to be difficult, since in literature information are lacking in important practical details, when available. A study recommends tetramethyl orthosilicate as crosslinking agent and methylamine as guest gases source (Gunawardane et al., 1987). We have employed the safer tetraethyl orthosilicate as crosslinking agent and methylamine as guest gasent and chemically purified water as medium.

Quantitative XRD (X-Ray Diffraction) analyses on powdered synthesized material have revealed MEP with less than 10 wt.% amorphous silica. Rietveld refinements, done with a cubic symmetry, and Raman spectra have suggested that methylamine may have entered inside the cages, despite its size. DSC (Differential Scanning Calorimetry) has shown a reversible reaction between -40 and -20 °C. TGA (Thermal Gravimetric Analysis) has shown two consecutive processes of mass loss, resulting in a whole mass variation less than 3 wt.% between 50 and 880 °C. A study of interactions between guest molecules and host framework cannot be done with single crystal XRD, due to synthesized MEP twinned nature (as the natural one), so neutron spectroscopy investigations are planned.

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## Dehydration and high temperature behavior of zeolite ferrierite: in situ synchrotron X-ray powder diffraction study

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Keywords: Zeolite ferrierite, thermal behavior, high temperature.

Zeolite dehydration has been widely studied because the sorptive and catalytic properties of these materials are profoundly influenced by processes which occur at relatively high temperature (HT). The knowledge of the structural modifications induced by HT and the definition of the stability fields of these materials is fundamental to assure their persistence and effectiveness in technological applications. Here we discuss the thermal stability and dehydration dynamics of the natural zeolite ferrierite.

A sample from Monastir  $[(Na_{0.56}K_{1.19}Mg_{2.02}Ca_{0.52}Sr_{0.14})(Al_{6.89}Si_{29.04})O_{72} \cdot 17.86H_2O; a=19.2241(3)Å;$ b=14.1563(2)Å; c=7.5106(1)Å, V=2043.95(7)Å<sup>3</sup>] was gradually heated and investigated by thermogravimetric (TG) analysis and in situ synchrotron X-ray powder diffraction. TG analysis shows that water release starts from the very early stages of heating and is complete at 600°C. The results of the structural refinements performed by Rietveld method up to 670°C in both Immm and Pnnm s.g. did not reveal any significant differences, hence only the data obtained in the topological *Immm* s.g. are discussed. By continuously monitoring the thermal behavior, it is evident that ferrierite belongs to the group of zeolites that do not undergo neither phase transitions nor significant modifications of the framework upon dehydration. Upon heating to 670°C ferrierite from Monastir behaves as a noncollapsible structure displaying only a slight contraction of the unit cell volume (-3%). Moreover, the cell parameter reductions are anisotropic, more marked for a (Delta a=-1.6%) than for b and c axes (Delta b = -0.76%; Delta c = -0.70%). This anisotropic response to heating is interpreted as due to the presence, in ferrierite framework, of five-membered ring chains of SiO<sub>4</sub> tetrahedra that confer to the structure a higher rigidity along b and c. Upon dehydration we observe: i) the gradual water loss - starting from the molecules hosted in the 10MR channel - is almost complete at 670°C, in good agreement with the TG data; ii) as a consequence of the decreased water coordination, Mg and K migrate from their original positions moving from the center of the channel towards the walls, to find a better coordination with the framework oxygen atoms.

Beyond providing information on the thermal stability and heating behavior of natural ferrierite, the results of this work allow a comparison with the dehydration kinetics and mechanisms of the corresponding synthetic phases, contributing in identifying the role played by framework and extraframework composition on the high-temperature behavior of porous materials with FER topology. Moreover, the information on the thermal behavior of natural ferrierite can be exploited to predict the energetic performances of analogous synthetic counterparts, namely "zeosil-electrolyte" systems, under non ambient conditions.

## Crystal-fluid interactions in open-framework silicates

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Keywords: zeolites, crystal-fluid interaction, pressure.

The structural evolution of microporous materials compressed hydrostatically in a fluid is drastically affected by the potential crystal-fluid interaction, with a penetration of new molecular species through the zeolitic voids in response to applied pressure.

On the basis of recent experimental findings and computational modelling studies, it was observed that when no crystal-fluid interaction occurs, the effects of pressure are mainly accommodated by tilting of (quasi-rigid) tetrahedra around the bridging O atoms. Tilting of tetrahedra is the dominant mechanisms at low-mid *P*-regime, whereas distortion and compression of tetrahedra dominate the mid-high *P* regime. The deformation mechanisms are governed by the topological configuration of the tetrahedral framework, but the compressibility of the cavities is controlled by the ionic and molecular host content, resulting in different unit-cell volume compressibility in isotypic structures. One of the most common deformation mechanisms in zeolitic framework is the increase of channels ellipticity.

Not all the zeolites experience a *P*-induced intrusion of new monoatomic species or molecules from the *P*-transmitting fluids. For example, natural zeolites, with well-stuffed channels at room conditions, tend to hinder the penetration of new species through the zeolitic voids. Several variables govern the sorption phenomena at high pressure: the "free diameters" of the framework cavities, the configuration of the extra-framework population, the partial pressure of the penetrating molecule in the fluid (if mixed with other non-penetrating molecules), the rate of *P*-increase, the surface/volume ratio of the crystallites under investigations, the temperature at which the experiment is conducted. The most recent findings allow us to provide an overview of the intrusion phenomena of monoatomic species (*e.g.*, He, Ar, Kr), small (*e.g.*, H<sub>2</sub>O, CO<sub>2</sub>) and complex molecules, along with the *P*-induced polymerization phenomena, (*e.g.*, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>O, C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, BNH<sub>6</sub>, electrolytic MgCl<sub>2</sub>·21H<sub>2</sub>O solution), with potential technological and geological implications.

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Gatta, G.D., Lotti, P. & Tabacchi, G. (2017): The effect of pressure on open-framework silicates: elastic behaviour and crystal-fluid interaction. Phys. Chem. Minerals, 45, 115-138.

#### Brønsted acid sites location and thermal stability of NH<sub>4</sub>-exchanged omega zeolite

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Keywords: Omega zeolite, NH4 exchanged precursor, neutron and X-ray diffraction.

Due to their structural features, e.g., the pore system which highly affects their selectivity, acid zeolites are considered of great importance as catalysts in cracking processes of oil refining (isomerization and hydrocarbons cracking). Catalytic activity of acid zeolites depends on the presence of the so-called Brønsted acid sites, *i.e.*, protons bonded to framework oxygen atoms. In order to evaluate their catalytic efficiency, the determination of nature, density, strength and location of Brønsted sites is of particular relevance. Since hydrocarbons catalysts are employed at high temperature, and their molecular sieve features as well as sorptive and catalytic properties are enhanced by heating, the thermal stability of those compounds must be accurately investigated. Zeolitic catalysts characterization through X-ray and neutron diffraction at non-ambient conditions is one of the best analytic tool to prove both their efficiency and stability and characterize their shape selectivity. In this contribution, a NH4-form omega zeolite was characterized to disclose the presence of acid sites and investigate temperature induced modifications. The as-synthesized omega zeolite (a mazzite analogue with formula Na<sub>66</sub>TMA<sub>18</sub>(H<sub>2</sub>O)<sub>222</sub>[Al<sub>84</sub>Si<sub>276</sub>O<sub>72</sub>]-MAZ) was previously studied by Martucci et al., 2003. Its NH<sub>4</sub>-exchanged form  $(Na_{2.4}TMA_{0.9}(H_2O)_{4.2}(NH_4)_{20}[Al_{8.4}Si_{27.6}O_{72}]$  was obtained through cationic exchange at Room <sup>4</sup> Temperature (RT) and at 90°C, 3-times each. Powder patterns were collected at the GILDA-BM8 Beamline (ESRF) from RT to 900 °C (heating rate: 5°C/min) and at the D2B Beamline (ILL) at 4 K, and Rietveld refinements were performed through the GSAS-EXPGUI package. Obtained results clearly show: 1) a progressive TMA template and NH<sub>4</sub> release induced by the heating process; 2) a NH<sub>4</sub> migration highlighted by O-O shortening and T-O-T variations within 6MR, 8MR units and the gmelinite cage which progressively become more distorted on heating. Such structural deformation is particularly highlighted by 1) the variation of T-O2-T angles (*i.e.*, progressive shift of O2 framework oxygen towards the centre of gmelinite cage; and 2) a decreasing of O1-O2 bond distances (due to Brønsted acid sites formation on O2 oxygen atom). Moreover, neutron refinements revealed a disordered Si-Al distribution within tetrahedral sites with a preferential occupation of  $Al^{3+}$  for the T2 site with respect to T1. Although non-reversible framework modifications occur, all the information here gained reveal the omega zeolite as performing hydrocarbons catalyst even at high temperature: indeed, it is stable up to 700°C.

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## An *in situ* HT-HP single crystal X-ray diffraction study of armstrongite, a microporous zirconium silicate

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Keywords: armstrongite, dehydration, compressibility, in situ HT-SCXRD.

Armstrongite,  $CaZr[Si_6O_{15}] \cdot 2H_2O$ , is a natural "zeolite-like" Zr-silicate with a heteropolyhedral framework consisting of SiO<sub>4</sub> tetrahedra and ZrO<sub>6</sub> octahedra that form cavities occupied by Ca-exchangeable cations (Mesto *et al.*, 2014). The behavior at non ambient conditions of armstrongite from Khan Bogdo deposit (Gobi, Mongolia) was studied by *in-situ* High Temperature Single Crystal X-ray Diffraction (HT SCXRD), both in air and under dry conditions up to 500°C and 375 °C respectively, and by *in-situ* High Pressure Single Crystal X-ray Diffraction (HP SCXRD) using synchrotron X-ray diffraction data (collected up to 8.01 GPa), a diamond anvil cell and the mix methanol:ethanol:water as hydrostatic pressure-transmitting fluid.

On heating an abrupt discontinuity in the trend of the cell parameters and unit-cell volume occurs at  $T = 275^{\circ}C$  in dry condition and at  $T = 450^{\circ}C$  in air. The cell volume decreased by ~7.5%, compared to that measured at RT, and is compatible with the loss of the two water molecules. The dehydrated phase (solved and refined at 275°C only under dry conditions) exhibits the same space group (C2/m) as RT armstrongite, significantly shortened *a* and *b* cell dimensions, increased  $\beta$  angle, and smaller unit-cell volume (*a*=13.406(3), *b*=13.752(3), *c*=7.811(2) Å,  $\beta$ =110.22(3)°, V=1351.3(5) Å<sup>3</sup>) with respect to the hydrated phase (*a*=14.0135(7), *b*=14.1234(6), *c*=7.8388(4) Å,  $\beta$ =109.401(4)°, V = 1463.4(1) Å<sup>3</sup>) at RT. The process is also accompanied by the distortion of the cavities as a consequence of Ca splitting and positional disorder of tetrahedral framework oxygens. The dehydration/rehydration process of armstrongite is completely reversible as also found from previous HT XRPD investigation (Schingaro *et al.*, 2018).

HP SCXRD data show a first-order phase transition between 4.01(5) and 5.07(5) GPa. In the high-pressure polymorph, the unit-cell volume triplicates. The bulk compression of armstrongite is mainly accommodated through the tilting of both SiO<sub>4</sub> tetrahedra and ZrO<sub>6</sub> octahedra around the shared oxygen hinges. The high-P polymorph of armstrongite is found to be stiffer ( $K_{V0}$  increase of ~ 66%), and a remarkable change of the elastic anisotropic scheme occurs. No evidence of crystal-fluid interaction, with a selective sorption of molecules of the pressure-transmitting fluid through the cavities, was observed.

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## Structural evidence of herbicide (2-ethyl-6-methylaniline) adsorption from aqueous solution in synthetic ZSM-12 zeolite

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Keywords: ZSM-12, herbicide, adsorption.

Pesticides are include in the hazardous substances class and they are transferred into the environment through various pathways (e.g. surface runoff, subsurface and groundwater flows) (Levitan, L., 2000; Boithias, L. et al., 2011). According to the current directives regarding drinking water quality, an individual species of pesticide should be not present in the water body over the standard concentration of 0.1 g/l, while the overall concentration of different kind of pesticides should not exceed 0.5 g  $L^{-1}$  (EC, Directive 98/83/EC, 1998). The recent wide use of these pollutants in the intensive farming is causing of serious environmental problem due to the toxicity of pesticides for the animal and human health (Otero R. et al 2012). In particular, more attention should be done regarding the family of chloroacetanilides compounds and among them, Metolachlor (C15H22ClNO2), and their metabolites (e.g. 2-Chloro-N-(2-ethyl-6-methylphenyl)acetamide, 2-ethyl-6-methylaniline) are frequently detected in surface and subsurface water. For that reported above, this work is devoted to test the adsorption capability of synthetic ZSM-12 zeolite toward 2-ethyl-6-methylaniline (C<sub>2</sub>H<sub>5</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)NH<sub>2</sub>, labelled EMA). The removal from water solution of this degradation product of Metolachlor is evaluated through the use of combining chromatographic, thermogravimetric and synchrotron X-ray powder diffraction techniques. Specifically, the synchrotron radiation data was collected at the MCX beamline of Elettra-Synchrotron (Trieste) using a fixed wavelength (0.827Å). Initially, the structure of as synthesize material was characterized, by Rietveld refinemet, in order to verify the presence of the template 6-azonia-spiro-[5,5]-undecane as structure directing agent (ZSM-12-SDA). After calcination in order to remove the template, the ZSM-12 sample was loaded with EMA compound. The EMA concentration in the aqueous solution was determined by Headspace Gas Chromatography coupled to Mass Spectrometry (HS-GC-MS). The adsorption isotherm, determined using the batch method, highlight a very fast ZSM-12 adsorption kinetics. Afterward, the adsorption capacity of ZSM-12 was evaluated also with the Rietveld method. Based on the analysis of difference Fourier maps, EMA molecules was localised in the ZSM-12 channel and the refined occupancies suggest the adsorption of about 4 EMA molecules per unit cell, in very good agreement with the weight loss given by TG analyses (performed in air using an heating rate of 10°C/min, from room temperature up to 900 °C) and with the saturation capacity determined by the adsorption isotherms. To summarized, the obtained results (rapid kinetic combined with the good adsorption capacity) suggest that the ZSM-12 zeolite may be suitable to remove the tested pesticide from water and could represent a promising future candidate as an environmentally friendly alternative in the removal of acetanilides compounds.

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## Tailoring structure and acidity properties of zeolites for biomass valorization

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Keywords: Zeolite-type catalysts, biomass valorization, biodiesel.

Zeolite-type catalysts may be considered one of the key catalytic materials with the largest range of industrial applications for the production of fuels and chemicals (*Corma, 1997*). Recently, the changing scenario for energy and chemicals production has fostered the extension of the consolidated role of zeolite catalysis in crude oil refining also to biomass conversion (*Abate et al, 2016; Lanzafame et al, 2014*). Nevertheless, the bulky dimension of biomass derivatives and the wide nature of their functionalities, requires zeolites containing easily accessible active sites with controlled and moderated acidic strength to avoid the possible secondary reactions (*Lanzafame et al., 2015*).

In this contribution, the role of structure and acidity of zeolite catalysts in the selective etherification of the biomass derivative 5-hydroxymethylfurfural (HMF), a reaction of industrial relevance for the production of biodiesel additives, is discussed. The catalytic activity of BEA, MFI and Silicalite-1 zeolites in the ammonium and protonic form has been studied in the above cited reaction. The study of samples acidity confirms that the selectivity to the main reaction products is driven by the different nature and amount of Lewis and Brønsted acid sites, respectively. In particular, the ammonium-exchanged form of zeolites presents a higher selectivity to 5-(ethoxymethyl)furan-2-carbaldehyde (EMF), a high performing biodiesel additive, in comparison with the corresponding protonic form, particularly for BEA structure. A critical condition for enhanced catalytic performances is that dissociated ammonia remains in the zeolite cages, and may be reversibly re-adsorbed. Thus likely, the dissociated ammonia cooperates in the reaction mechanism or induces a confinement effect.

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## Zeolites for environmental purposes: storage and controlled delivery of CO, in FAU zeolties

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*Keywords*: nano-sized zeolites, FAU zeolites, CO<sub>2</sub> storage.

The demand for porous materials able to capture carbon dioxide is costantly increasing as the interest in zeolite applications in environmental and biological fields, including storage and controlled delivery of gases in biological systems (Mintova et al., 2015, Lehman,Larsen). The properties of nano-sized zeolites, provide new possibilities to exploit adsorption, reaction of guest molecules such as  $CO_2$ ,  $NO_x$  and  $O_2$  and reversible adsorption when controlled gas delivery is required. In this study, we report the results of experiments aimed to understanding  $CO_2$  adsorption/desorption mechanism in Na-X and Na-Y (FAU) zeolites carried out combining *in situ* high resolution synchrotron X-ray powder diffraction and IR spectroscopy.

The Rietveld structural refinement, along with IR data revealed that a portion of  $CO_2$  molecules is chemisorbed in the form of carbonates inside the super-cage of the faujasite structure. Overall, the formation of carbonates or bicarbonates (influenced by the presence of some residual water molecules) is clearly promoted in Na-X while in Na-Y sample most molecules are physisorbed. The pumping of Na-X has only a weak effect on carbonates (most of the molecules remains in the pores), while the HT treatment (250° C) results to be more effective in the removal of carbonate from Na-X supercage. For Na-Y sample, where most of the molecules are physisorbed and coordinated to Na cations or framework oxygen atoms, the pumping seems to be more effective and more than half of the molecules are released.

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### Session S27

## **Environmental and medical mineralogy:** from molecular to macro scale processes

Conveners AND CHAIRPERSONS Elena Belluso (Università di Torino) Pilario Costagliola (Università di Firenze) Franco Frau (Università di Cagliari)

# New tools and analytical procedures for the evaluation of asbestos-related health risk in naturally occurring asbestos (NOA)-rich areas

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Keywords: NOA, SEM-EDS analysis, EHS risk.

The occurrence of naturally occurring asbestos (NOA) in excavation areas represents a common and yet unexplored problem in Northern Italy, especially in the Alpine zone and the Alps-Apennines junction. The construction of large infrastructures requires an enhanced geological risk evaluation to assure workplace safety from asbestos. Furthermore, the disposal of asbestos-polluted rock and soil introduces significant handling costs that must be carefully estimated in the preliminary phases of work engineering.

A proper risk assessment of asbestos requires, at first, a detailed geological model representative of the possible occurrence of NOA. The geological model requires in turn a representative sampling strategy which, combined with a correct analytical approach, enables to estimate, within reasonable approximations, the content of naturally occurring asbestos before excavation activities take place. During excavation, NOA quantification is also required to enforce proper environment, health and safety (EHS) procedures for reducing workers' exposure and managing waste and air emissions. Nevertheless, EHS regulations for working in asbestos-bearing natural materials are still not exhaustive, because of the great complexity of the matter and uncertainties in geological risk definition.

This work describes the crucial elements required to achieve a good asbestos risk analysis, based on detailed structural field surveys, integrated with borehole core analysis and mineralogical analysis, aiming at identifying homogeneous "petro-structural facies" on the basis of structural and lithological criteria. Homogeneous litho-structural domains are mapped at proper scale and sampling program is planned. Since the quantification of NOA still requires some criteria to be unambiguously defined, including the definition of "fiber", a special attention was devoted to systematically categorize asbestos fiber appearance under electron microscopy, including ambiguous objects, such as non-divided bundles and nanofibers with sub-micrometric diameter. The necessity to improve the quantitative determination of NOA with innovative approaches, such as automatic microscopic analysis that yield results with increased accuracy and reproducibility, was strongly envisaged and a new method proposed (Cossio et al., submitted).

This work represents a first attempt to draw guidelines for the analysis of asbestos-bearing natural materials, which is fundamental to evaluate the geological risk linked to NOA in order to lead excavation works on site and enforce EHS procedures.

Cossio, R., Albonico, C., Zanella, A., Fraterrigo-Garofalo, S., Compagnoni, R. & Turci, F. Innovative unattended SEM-EDS analysis for asbestos fiber quantification, Talanta, under review.

# Combining synchrotron radiation phase-contrast and fluorescence tomography to reveal the morphology and elemental composition of asbestos bodies in human lungs

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Keywords: asbestos, bodies, human lungs.

Once penetrated into the lungs, asbestos induces an in vivo biomineralisation process that leads to the formation of a ferruginous coating embedding the fibres, which is believed to be responsible for the high toxicological outcome of asbestos. Lung tissue of two former workers of an asbestos plant located in the Piedmont region (NW Italy), who have been subjected to prolonged exposure to crocidolite asbestos, was investigated using imaging and spectroscopic nano-probe techniques exploiting synchrotron radiation. These techniques have several advantages compared to the same techniques based on conventional X-ray sources. In particular, X-ray Phase-Contrast and X-ray Fluorescence Computed Tomography (respectively XPC-CT and XRF-CT) can nowadays be operated at resolutions down to 10nm and a sub-ppm sensitivity (Cedola et al., 2017; De Samber, 2018) and have the ability to image law absorbing materials with similar densities, as is the case of biological tissues. Besides the 3D morphology, the combination of XPC-CT and XRF-CT allowed obtaining the local thickness and mass density of the samples, and, therefore, a reliable elemental quantification (Gramaccioni et al., 2018). The distribution of K and of elements heavier than Fe (Zn, Cu, As, Ba, and Sr) in the asbestos bodies (AB) was observed for the first time. The distribution of Si suggested the incipient dissolution of the inner fibre, and that of Zn, Cu, As, and Ba, indicated that the AB are efficient scavengers for these species, in agreement with the uptake ability of the mineral core of ferritin or hemosiderin (ferrihydrite). XANES spectroscopy indicated that Fe is in the 3+ oxidation state, and confirmed that it is present in the form of ferrihydrite. Comparison between AB studied upon removing the biological tissue by chemical digestion with NaClO, and those embedded in the original lung tissue, allowed understanding to what extent the digestion procedure altered their chemical composition. A model was proposed to describe the growth of the AB in the biological tissue (Bardelli et al., 2017).

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#### Mercury emissions from Herbaria of the University of Florence Natural History Museum

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Keywords: Herbaria, mercuric chloride, Hg0 diffusion.

The most common threat for herbarium specimens preservation is the diffusion of insects, larvae and fungi, which are defeated through the employment of chemicals. Up to 1970s, the most used preservative and biocide was mercuric chloride (HgCl<sub>2</sub>), latterly dismissed. Mercuric chloride decomposition causes Hg (especially Hg<sup>0</sup>) to diffuse in herbaria environments, which are generally characterized by poor ventilation with the outside. High levels of Hg may indeed persist decades after the HgCl<sub>2</sub> last treatment, then representing a potential health hazard for workers and visitors by inhalation of polluted ambient air.

In Italy, the employment of  $\text{HgCl}_2$  in herbaria is documented up to the end of 1930, when it was banned. In this study, new original data on the concentration and distribution of  $\text{Hg}^0$  in the main halls and worker offices of the Tropical Herbarium and the Herbarium of the Botanical Section of the Museum of Natural History both belonging to the University of Florence-Italy) are presented. These Herbaria, located in the city center, are among the largest in the world and the most important in Italy. Surveys were firstly conducted in July 2013 and then repeated in July and December 2017 to account for temporal and seasonal variation in Hg<sup>0</sup> by the employment of the Lumex (RA915M) instrumentation.

All the areas pertaining to Herbarium show Hg<sup>0</sup> concentrations well above (1 to 4 order of magnitude) the surrounding outdoor locations (University courtyard, Florence traffic congested squares and streets). Concentrations up to 8000 ng/m<sup>3</sup> Hg<sup>0</sup> were observed on the 2<sup>nd</sup> floor of the Herbarium, where the most ancient collections are presently stored. Particularly, peak levels of airborne Hg occur within the opening of specimen storage cabinets, which exceed the instrument's maximum detection limit (50,000 ng/m<sup>3</sup>). Lower Hg concentrations were observed at the 1<sup>st</sup> floor in all measurement campaigns. Here, lower and homogenized Hg levels were found during the 2017 campaigns, with respect to the 2013 one, as a consequence of the installation - in 2017- of a more efficient air-conditioning system.

Mercury airborne concentrations are in the range of those reported for other herbaria worldwide, testifying the persistence of this contaminant after almost 80 years from its last use, but lower than the current Italian permissible exposure limit which are established for the total Hg (Hgtot=Hg<sup>0</sup> + ionic Hg) concentrations. Further investigations for the determination of all Hg species are undergoing by our group in order to precisely assess the exposure routes of the workers and to minimize the Hg intake by adopting appropriate procedures.

### New data on the presence and distribution of Hg in the Paglia-Tiber fluvial system

Costagliola P.\*<sup>1</sup>, Rimondi V.<sup>1</sup>, Benvenuti M.<sup>1</sup>, Lattanzi P.<sup>2</sup>, Fagotti C.<sup>3</sup>, Marchetti G.<sup>4</sup>, Martinelli A.<sup>5</sup>, Mascelloni L.<sup>4</sup>, Paolieri M.<sup>1</sup> & Sconocchia A.<sup>4</sup>

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Keywords: mercury, Tiber, Paglia.

The presence of anomalously high Hg values in the Paglia-Tiber fluvial system (central Italy) has been known for some years (Gray et al., 2014, and references therein). In 2017, the Tiber watershed authority prompted a systematic study of the presence and distribution of this metal in various environmental segments of this important fluvial system. The regional environmental agencies (ARPA) of Tuscany, Umbria and Latium were charged to carry out the study, with consultancy by the Universities of Firenze (geochemistry) and Perugia (fluvial dynamics). We present here the first results of the geochemical study.

There are at least two potential Hg sources for the Paglia-Tiber system: the past mining activity in the Mt. Amiata district (the 3rd largest Hg district in the world), and the ongoing exploitation of geothermal energy. Benvenuti & Costagliola (2016) suggested that contribution from this last source is by far minor compared to mining activity. The first data of this study indeed confirm this suggestion. The highest values of Hg in sediments (up to 1,900 mg/kg) occur in the Siele and Stridolone watersheds, affected by the Siele and Cornacchino mines.

The concentration of Hg in sediments markedly decreases southward, most notably downstream of the Alviano dam, that acts as a physical barrier for Hg-bearing particulate. However, anomalous (i.e., beyond the 1 mg/kg Italian regulatory limit for residential soil) Hg values are documented in sediments and soil along a narrow band extending at least to Castel Giubileo, just north of Rome. A main goal of the study will be a reliable operational definition of this "contaminated" band.

By contrast, Hg contents in stream waters are consistently below the 1  $\mu$ g/L limit for drinking waters. However, fish contents in the Paglia river often exceed the recommended limits for human consumption, and suggest the opportunity of cautionary measures. On the other hand, Hg contents in vegetables grown on soils of the "contaminated" band apparently do not pose sanitary problems, assuming standard dietary habits.

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### Spectroscopic analysis of the artificial stone powders: chemical causes for their cellular toxicity

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Keywords: crystalline silica toxicity, EPR, XAS.

Artificial stone (AS) is a composite material realised assembling powders, and occasionally fragments, of natural stones with a binder. After the inlet of resins-based AS in the large scale production (lasting since 1986) the occurrence of silica-related diseases among the artificial stone workers (ASW) was claimed, associated to an extremely short latency, and an high severity of the diseases. It is believed that high levels of exposure to silica dust can hardly justify alone all clinical findings, thus supporting the idea that some intrinsic properties of this material can modulate the usual path for development of silicosis and auto-immune diseases. The present experimental study compares parent materials and their dusts, obtained from different production lines (where exposure for workers exceeded 100 times the TLV), to shed light on changes of AS through the manufacturing process, through a combined XRF chemical and EPR and XAS spectroscopic investigation. As a result, we point out the extremely wide variability of the composition-processed materials, the occurrence of chemical signatures impressed by the processing techniques, the occurrence of cristobalite in selected samples, and the generation and preservation of radicals associated to the lysis of the Si-O chemical bond inside the resin coated respirable crystalline silica particles. This evidence was never observed in industrial silica-bearing before. On these bases, our investigation sets the ground for stating that the processing of the AS in stone workshops and industries is able to create respirable dusts with peculiar physical and chemical properties, to be correlated to the observed clinical evidences.

#### Fluoride removal from water by Layered Double Hydroxides (LDHs)

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Keywords: layered double hydroxides, water defluoridation.

The usual consumption of drinking water with high fluoride (F<sup>-</sup>) concentration, over the limit of 1.5 mg/L set by the World Health Organization (WHO 2011), causes dental and skeletal fluorosis and is a serious health issue that affects the rural areas of the East African Rift Valley.

This work contributes to the *Horizon*2020 FLOWERED project (*de-FLuoridation technologies for imprOving quality of WatEr and agRo-animal products along the East African Rift Valley in the context of aDaption to climate change*) for the development of a low-cost technology for the defluoridation of drinking water through sorption methods by using layered double hydroxides (LDHs), a group of minerals with a high potential for the treatment of contaminated water (Lv et al., 2006).

LDHs have general stoichiometry  $M^{2+}_{1-x}M^{3+}_{x}(OH)_2(A^{n-})_{x/n}$  ·mH<sub>2</sub>O. Their structure consists of octahedral brucite-like layers positively charged as a consequence of the partial substitution of bivalent metals  $(M^{2+}=Mg^{2+}, Zn^{2+}, Ca^{2+}, etc...)$  with trivalent ones  $(M^{3+}=Al^{3+}, Fe^{3+}, etc...)$ , alternating with negative interlayers containing anions  $(A^{n-}=CO_3^{-2-}, SO_4^{-2-}, Cl^{-})$  and variable quantity of water (Cavani et al., 1991).

LDHs can remove dissolved anions from solutions through the anion exchange or by rehydration after calcination. In the first case, the anions dissolved in solution replace those present in the interlayer of untreated LDHs; instead, in the second case, the mixed oxides obtained from LDHs calcination, when immersed in solution, uptake anions in the interlayer during the rehydration and the reconstruction of the LDHs lamellar structure. Moreover, great advantage can derive from the use of LDHs for several cycles of regeneration.

LDHs with different cationic ( $M^{2+}=Mg^{2+}$ ,  $Zn^{2+}$ ;  $M^{3+}=Al^{3+}$ ,  $Fe^{3+}$ ) and anionic ( $A^{n-}=CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $Cl^{-}$ ) compositions have been synthesized, with a coprecipitation method at constant pH, and sorption tests have been carried out to assess the LDHs F<sup>-</sup> removal capacity, the effect of coexistent anions in solution and the F<sup>-</sup> removal capacity of regenerated LDHs.

Results show that calcined carbonate LDHs can remove up to 43 mg of  $F^-$  per g of sorbent and that, after four regeneration cycles, the removal capacity is still 80%. However, the  $F^-$  removal capacity can significantly decrease in the presence of high concentration of coexistent anions, especially carbonate species at the high pH values reached during the experiments. Next study will be addressed to obtain the best performance of LDHs for the  $F^-$  removal from natural water.

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### XRPD quantification of naturally occurring asbestos (NOA) in Serpentinites: influence of ball milling on the diffrattometric response

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Keywords: Naturally Occurring Asbestos, Serpentines, Sample Preparation.

The environmental hazard raised by naturally occurring asbestos (NOA) during construction project, mining or tunneling in asbestos-rich natural areas is a major concern for workplace safety and environment protection agencies (Turci et al., 2016; Bloise et al., 2017). To estimate correctly the risk associated to NOA, new analytical tools to quantify the concentration of asbestos in its forming rock are strongly envisaged. X-Ray powder diffraction (XRPD) suitably determines the relative abundance of each mineral phase in a polycrystalline material, but the sample preparation is a critical step particularly for asbestos, because mechanical grinding may alter the crystal lattice and the fibrous form induce sample preferential orientation, in turn affecting the diffractometric response (Ocella, 1994; De Stefano et al., 2000). The aim of this work is to optimize sample ball milling time to minimize iso-orientation yet collecting an intense diffractometric response. A lizarditic serpentinite containing chrysotile, the most common asbestos mineral in Western Alps, was ground with isopropyl alcohol up to 10 minute, using a tungsten carbide ball mill equipped with two 25ml jars (around 1 gram of sample each) and 25 s<sup>-1</sup> oscillation frequency. Rutile (TiO<sub>2</sub>) was added as reference standard. The samples' diffractograms were recorded according to the methods in previous works (De Stefano et al., 2000). Particle size and shape distribution were obtained via automated SEM-EDS image analysis. Strong preferential orientation and large particle size dispersion were observed for grinding time shorter than 1 minute. Longer grinding times induced a time-depended decrease of peak intensity due to the partial amorphization of chrysotile. Our results show that a good diffractometric response and an optimal particle size distribution can be obtained with 1 minute grinding time. This fast comminution procedure yielded XRPD suitable asbestos sample, without texture effect or loss of crystallinity. The method is proposed as the standard sample preparation protocol for routine quantitative analysis of asbestos in natural settings.

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# From octacalcium phosphate (OCP) to fluorapatite, a new method for defluoridation of drinking water

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Keywords: defluoridation, East African Rift Valley, octacalcium phosphate.

Geogenic contamination of fluoride (F<sup>-</sup>) in ground water is one of the major problems of the water crisis of the 21<sup>st</sup> century, affecting about 200 million people over 24 countries (Kumari & Khan, 2017). The World Health Organization recommends concentration of F<sup>-</sup> < 1.5 mg/L for drinking water, in that higher concentrations cause several diseases, such as the most common mottled enamel, osteoporosis and crippling skeletal fluorosis (WHO, 2010).

The aim of this work, in the framework of the FLOWERED project (a Horizon2020 European funded project: Grant Agreement - N. 690378) (www.floweredproject.org), is to develop a low-cost defluoridation technique addressed for rural populations of the East African Rift Valley.

The octacalcium phosphate (OCP), a calcium phosphate with general formula  $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$ , is a precursor of apatite group which includes hydroxylapatite  $Ca_5(PO_4)_3OH$  (HAP) and fluorapatite  $Ca_5(PO_4)_3F$  (FAP).

OCP is a very unstable phase in aqueous solutions that, in the presence of F<sup>-</sup> or at pH > 7.4, transforms in an epitaxial growth of HAP-FAP through sub-solidus reaction (Zhan et al., 2005). The stoichiometric fluoride uptake capacity of the reaction OCP -> FAP is 34.4 mg F<sup>-</sup>/g OCP.

The potential of OCP in fluoride removal from both synthetic solution and natural water has been tested through sorption experiments performed in batch mode: vials of 50 ml with 200 mg of OCP and different initial concentration of fluoride (40, 60, 80, 120, 140 mg/L F<sup>-</sup>) have been placed on a rotor at 40 rpm for different time of reaction (from 0.5 to 24 hours). The possible effect of existing co-anions in solution was tested repeating the removal experiment with fluoride molar equivalent of Cl<sup>-</sup>, OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>.

The results show that the equilibrium of the reaction is reached within 8 hours; the empirical removal capacity ( $Q_e$ ) ranges between 25.7 and 28.6 mg F<sup>-</sup>/g OCP. No significant variations of  $Q_e$  are observed, neither in the presence of Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>, nor at different pH conditions (pH = 7, 8, 11.25). The experimental data, fitted with the Langmuir isotherm model and the pseudo-second-order kinetic equation, provide a theoretical maximum sorption capacity ( $Q_{max}$ ) of 29.6 mg F<sup>-</sup>/g OCP at 20 °C. All the solutions after the treatment reach a circum-neutral pH of 7.01-7.26.

Further development of this research will be focused on the realization of effective, low-cost filters to be tested in the rural areas of the East African Rift Valley.

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### Fumarolic alteration products of three hydrothermal areas of Greece: Chemical characterization and environmental impact

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Keywords: Hydrothermal alteration products, sulfates, toxic metals.

Samples of efflorescences and encrustations of hydrothermal origin have been collected at three fumarolic areas in Greece. The three sites are Sousaki, Thiafi (Methana) and Kokkino Nero (Kos) and all belong to the South Aegean Active Volcanic Arc. Samples were analysed for their mineralogical (XRD and SEM-EDS) and chemical composition. Solutions obtained from both mineralization with HNO<sub>3</sub> and leaching with distilled water, were analysed for major (ICP-OES), minor and trace metals (ICP-MS) and for sulfate contents (IC). Results show that their composition is mainly controlled by the petrological composition of the substrate (ultramafic rocks at Sousaki, felsic volcanic rocks at Methana and low-grade metamorphic rocks at Kos). The microenvironmental conditions (humidity, oxidizing or anoxic, exposed or sheltered from meteoric agents) as well as the rainfall regime of the area play also an important role. The presence of highly soluble sulfate minerals with elevated contents of many metals further underscores the significant influence of hydrothermal activity on elements' mobility. The sometimes very high concentrations in toxic elements like Al, As, Co, Cr, Ni evidence also a potential environmental impact.

### Mineral evolution at geosphere-biosphere interface: investigation on the endemic shrub Helichrysum microphyllum Cambess. subsp. tyrrhenicum Bacch., Brullo & Giusso growing in abandoned mining area

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Keywords: Helichrysum microphyllum, rhizosphere, biomineralization.

Beyond the fundamental interaction between water and rock, the active role of living organisms in the formation of new minerals stable at the Earth's surface must be considered (Velde & Barré, 2009). Transformation of primary minerals caused by biological degradation is up to several orders of magnitude faster than transformation of minerals due to water-rock interaction. In the rhizosphere, root exudates and associated soil microorganisms promote mineral alteration, precipitation of new phases, and the transfer of macro- and micro-nutrients from minerals to plants (Cabala et al., 2004).

The reported processes allow plant utilization in remediation actions through phytostabilization strategies. In our study we selected an endemic shrub, *Helichrysum microphyllum* Cambess. subsp. *tyrrhenicum* Bacch., Brullo & Giusso (hereafter *H. tyrrhenicum*), growing on a Zn-Pb ore flotation tailings pond (Campo Pisano mine, Sardinia, Italy). Quartz and dolomite were detected in the bulk soil and in the rhizosphere, whereas phyllosilicates and pyrite were found only in the rhizosphere. The bulk soil is characterized by the presence of goethite, gypsum and jarosite. Pyrite probably precipitates at the soil-root interface because of the synergistic action of roots and associated microorganisms thus controlling rhizosphere mineralogy. In *H. tyrrhenicum* roots we detected the same minerals of the rhizosphere, suggesting that minerals are embedded in plant tissues.

Soil-to-plant transfer of Zn by *H. tyrrhenicum* was characterized by Zn accumulation in plant roots  $(Zn_{roots} 2900-4000 \text{ mg/kg})$ . The Zn coordination environment changes from the rhizosphere (mainly hydrozincite, Zn sulfate and Zn acetate) to the plant roots (mainly Zn apatite) pointing out an active role of the physiological mechanisms of the plants in incorporation of Zn into the biological tissues and biomineralization (Medas et al., 2017). These finding strongly motivate future researches aimed to investigate the reaction mechanisms governing mineral evolution in the rhizosphere and the reaction kinetics in the presence or absence of mycorrhiza and soil microbes.

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# Tracing mercury mobility and distribution in the Abbadia San Salvatore legacy mercury mine area using mercury isotope ratios and concentrations

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Keywords: mercury isotope, pollution, environment, Monte Amiata.

Persistent mercury (Hg) impact from legacy mines continues to present risk to the environment and human health globally. The Monte Amiata Hg district in Southern Tuscany, Italy was one of the five largest Hg districts in the world. Mining of Hg began in the region during the Roman era with modern mining beginning in the mid-1800s and concluding in the early 1980s which resulted in the occurrence of elevated Hg in the surrounding ecosystem. The study area focused in the vicinity of Abbadia San Salvatore mine (ASSM) as it was the major Hg processing facility for many mines in the district and considered a primary source for elevated Hg. Heavy historical Hg production and large deposits of mine-waste calcines are still potential sources of elevated Hg in this area. The extraction of Hg from cinnabar was carried out via the roasting of ore using two primary furnace types. Initially, Čermak-Špirek shaft type and tower furnaces were used which were later replaced by Gould and Pacific type furnaces. The ore was roasted at 600-700°C to volatize Hg to gas which was recovered via condensation. Mass dependent fractionation (MDF) of Hg isotope ratios and variation in Hg concentrations resulting from the processing of cinnabar ore has been reported for minewaste calcines. Elevated concentrations of Hg in the extensive mine-waste calcine piles in ASSM possess the potential of releasing Hg into the local environment over a sustained period of time. The differences in extraction efficiency of Hg from cinnabar ore of different grain size and different furnace types resulted in variations of Hg concentration and isotopic composition in the mine-waste calcines (Cermak-Spirek calcine d<sup>202</sup>Hg average of 0.52‰ and concentration range of 32 to 1500 ug/g; Gould and Pacific d<sup>202</sup>Hg average of -0.58 and concentration range of 25 to 130 ug/g). Mass independent fractionation (MIF) has also been reported for Hg isotope ratios with a positive shift in  $D^{199}$ Hg and  $D^{201}$ Hg attributed to methylation and demethylation, and a negative shift in D199Hg and D201Hg related to photochemical reactions. The contribution of Hg from the weathering of legacy mine-waste calcine piles as well as initial Hg contribution from historical Hg ore processing has resulted in a wide range of Hg concentrations (0.48 ug/g to 1500 ug/g) and d<sup>202</sup>Hg and D<sup>199</sup>Hg isotopic compositions (-1.96% to 0.95%, -0.30% to 0.25% respectively). We will present an overview of Hg distribution and mobility using concentration and isotopic composition measured for a wide range of samples (cinnabar ore, calcines, sediment, soils, geothermal water, and fish) collected in the ASSM area.

### Heavy metals in barks: a protocol for sampling and analysis

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Keywords: Mercury, tree bark, sampling and analysis protocol.

Biomonitoring is a valuable assessment tool to monitor the distribution of heavy metals (HM) in the atmospheric environment. Tree barks are excellent adsorbents of airborne pollutants. However, their use is still limited, particularly because of the absence of well-defined protocols for sampling and analysis.

The present study aims to evaluate some sampling variables that may affect HM analysis in barks, like: i) sample orientation; ii) sample height; and iii) sample thickness. A better understanding of these variables will help to expand the use of barks in biomonitoring studies. For this purpose, mercury (Hg) is a key element since it may be transported both as particulate and as gaseous phase (Hg<sup>0</sup>).

In this work, tree barks of Black Pine (*Pinus nigra* J.F. Arnold) and surrounding soils were sampled in the Mt. Amiata region (Southern Tuscany Italy). In this area, past Hg mining activity (ended in 1980s) strongly affects airborne Hg concentrations, particularly in the mining site of Abbadia S. Salvatore. To account for Hg variations, different sampling sites were chosen within the Abbadia S. Salvatore mining area and in local reference areas. For each site, barks were collected at: i) two different heights, 70 and 150 cm; and ii) along the four cardinal points for each height. For all samples, Hg was determined in the first 1.5 cm of bark thickness; three samples were also analyzed longitudinally into bark to 3.5 cm to account for Hg variation in response to bark sampling depth.

Mercury in barks reached ~30 mg/kg, increasing in the mining area of Abbadia S. Salvatore. Lower values (down to 0.1 mg/kg) were found in the surrounding reference areas, suggesting the presence of a point source of contamination connected to past metallurgical activity at Mt. Amiata. Similarly, the highest concentrations in soils generally occurred close to Abbadia S. Salvatore (up to 500 mg/kg). Results, validated by statistical analysis (Kruskal-Wallis test), indicate that Hg content in barks is virtually unaffected by sample orientation, although barks were collected in a district where wind directions are rather focused. At Mt. Amiata, prevailing winds are from W with minor contributes from SE and NE. The homogenous distribution of Hg along the tree bark perimeter is particularly true for barks collected at 150 cm. Furthermore, although we generally document a correlation between Hg in bark vs Hg in soil, this is reinforced for samples collected at 70 cm, indicating that these samples are more influenced by local soil particle resuspension with respect to those collected at higher heights. Sampling at higher heights seems therefore preferable to exclude local-site effects affecting airborne Hg concentrations (i.e. soil resuspension).

Finally, Hg concentration is significantly lower in bark sampled deeper into the bark layers (3.5 cm deep), denoting a crucial importance to define a standardized bark thickness for the analysis of Hg and possibly other HM.

### Natural radioactivity measurements and radiological risk evaluation along the Calabrian coast (South Italy)

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Keywords: natural radioactivity, radiogenic exposure, human health.

The knowledge of the natural radioactivity levels and the consequent assessment of public health hazard continues is still an environmental and public concern. Natural radioactivity due to the radioactive families <sup>238</sup>U and <sup>232</sup>Th and <sup>40</sup>K provides the largest contribution to the dose received by the population. Radionuclides concentrations and their decay products are determined by both the rock types and the formation processes.

Many pocket beach placers outcrop along the Calabria coastline (South Italy) and are popular as tourist destination for summer holidays. Those sands conatin heavy-mineral with significant concentrations of radioactive elements thus representing a potential danger for the human health due to radiogenic exposure. This study aims to calculate the gamma dose rate, crucial to estimate the radiological risk from external irradiation, and the annual effective dose equivalent (AEDE) received from a three months stay (e.g. summer period) in the investigated beach. The study area is the Pizzo-S. Eufemia beach, produced by the slow dismantling process of the granitoid rocks belong to the Serre Massif that represents the linkage between the southern (Aspromonte Massif and Peloritani Mts) and the northern (Sila Massif and Coastal Chain) sectors of the Calabria-Peloritani Arc.

The radioactivity investigation was performed by a high resolution HPGe gamma-ray spectrometer. From the measured gamma-spectra, the average activity concentrations were determined for <sup>226</sup>Ra (in secular equilibrium with <sup>238</sup>U), <sup>228</sup>Ac (in secular equilibrium with <sup>232</sup>Th) and <sup>40</sup>K. In particular, for <sup>226</sup>Ra values ranged from 199.9  $\pm$  19.3 Bq/kg to 266.1  $\pm$  31.3 Bq/kg; for <sup>228</sup>Ac, from 1559.9  $\pm$  96.1 Bq/kg to 1832.5  $\pm$  112.7 Bq/kg and for <sup>40</sup>K from 238.6  $\pm$  47.5 Bq/kg to 276.6  $\pm$  45.6 Bq/kg. The absorbed dose rate and the effective dose rate outdoor were found to be in the range of 1045 -1240 nGy/h and 0.32 - 0.37 mSv/y, respectively.

To provide a full characterization of the heavy-mineral sand a multidisciplinary approach including Scanning Electron Microscopy (SEM-EDX), X-ray powder Diffraction (XRPD) and X Ray Fluorescence (XRF) has been used. The heavy mineral phases identified are magnetite, ilmenite, garnet, rutile and monazite. Bulk chemistry data put in evidence very high amount of Th in the range of 409 - 464 ppm.

The results of this study, also compared with values of other locations around the world, can be used as a baseline for future investigations about radioactivity background levels along the Calabria coastline and coupled with epidemiological studies to better evaluate possible health effects on the population.

# Session S28 Mineralogy, waste management and environmental pollution

Conveners AND CHAIRPERSONS Mario Tribaudino (Università di Parma) Luciana Mantovani (Università di Parma) Valerio Funari (ISMAR-CNR, Bologna)

#### Using RHA method for environmental problems: a case of study

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Keywords: Rank analysis, Phthalates, Environmental risk.

The RHA method is an informatics language that can be used to describe, grouping, organizing and for the accommodation of the composition of objects of any nature (Petrov, 2001). The method was developed by prof. Thomas Petrov from the St. Petersburg State University since 1971 and is implemented in PETROS-3 software package (author Moshkin S). The RHA system consists of three parameters: R - Rank formula, H - Entropy, A - Anentropy. The first parameter (R - the rank formula) is the succession of component symbols arranged according to their decreasing content. If components are chemical elements, the rank formula (Rchem) will correspond to a set of element symbols ranked in order of decreasing atomic percent (Krasnova et al., 2003). The other two parameters are used to discriminate, in term of order/disorder, object having the same Rank Formula. In particular: Entropy is essentially a measure of the complexity of the system, characteristic of the degree of uniformity of distribution of different components in a specific system; while Anentropy - is a measure of the "purity of the system (Petrov et al., 2016).

In general the method has been used successfully for the systematic of rocks. We have tried to use it in the environmental field to define a distribution model for phthalates in the seaside (Stoppa et al., 2017). We first ordered the data in term of decreasing molecular weight 390.56 (Di 2-ethylhexyl phthalate DEHP), 312.36 (Butyl benzyl phthalate BBP), 278.34 (Diisobutyl phthalate DIBP and Dibutyl phthalate DBP), 222.24 (Diethyl phthalate DEP) and 194.18 (Dimethyl phthalate DMP). Then, we ranked the components in function of the decrease in their concentration (rows). The method allowed us to highlight for each sampling area the relative abundance of the different phthalates ordered from the most abundant to the least abundant. In particular, we observed that high anentropy levels have to be associated with high phthalate content and indicate an impending phthalate risk associated with sediments near the mouth of most of the main rivers in the area. In conclusion, the RHA method represents a new statistical language that shows potential applications in geological and environmental fields.

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### Todorokite, Ranciéite and Birnessite from Serra D'Aiello (Southern-Italy): New mineralogical and geochemical data

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Keywords: manganese dioxides, Pollution, Calabria.

The knowledge on mixed Mn (II/III/IV) oxides is still unsatisfactory in a number of ways, despite their widespread occurrence in marine and terrestrial environments. Mn-bearing phases are highly reactive and are able to exert a strong control on the speciation, mobility and bioavailability of trace metals and micronutrients (e.g., Post, 1999).

This paper reports the results of a detailed study on the manganese dioxides occurring in the manganesiferous deposit outcropping in the Messinian sediments from the Serra D'Aiello area (Boni & Rolandi, 1975; Boni et al., 1976).

Terrains outcropping in Serra D'Aiello belong to the sedimentary successions of the Amantea Basin (Coastal Chain) characterized by two main sedimentary cicles: Tortonian-Messinian cycle (TMC) and Messinian-Lower Pliocene cycle (MLPC) divided each other by a compressive tectonic intramessinian event (Muto & Perri, 2002). The mineralization occurs widespread in sedimentary levels consisting of clayey-siltous alternations located to the top of MLPC. The mechanism of precipitation of manganese is due to the concentration of the mineral due to evaporation following to significant paleogeographic changes.

Nine samples have been characterized in detail through several techniques (XRPD, SEM/EDS, TEM/AEM, DSC/TG,  $\mu$ Rs). Results pointed out as all the collected samples contain birnessite (Na,Ca)0.5(Mn<sup>4+</sup>,Mn<sup>3+</sup>)2O<sub>4</sub>·1.5H<sub>2</sub>O, todorokite (Na,Ca,K,Ba,Sr)1-x(Mn,Mg,Al)6O<sub>12</sub>·3-4H<sub>2</sub>O and ranciéite (Ca,Mn<sup>2+</sup>)0.2(Mn<sup>4+</sup>,Mn<sup>3+</sup>)O<sub>2</sub>·0.6H<sub>2</sub>O in variable amount. However, SEM/EDS analysis show comparable compositions for all the nine samples highlighting a reservoir predominantly manganesiferous, while iron is quantitatively lower. The geochemistry of iron and manganese is very similar but in the Amantea basin there was complete separation between iron and manganese during alteration and deposition. The most reliable hypothesis is that there was a segregation at the origin, with a release of manganese much greater than iron.

Although manganesiferous deposits represent an important economic resources, they can play an important role on the groundwater geochemistry (Vespasiano et al., 2012) resulting dangerous for environment and human health.

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### Biomonitoring of air pollution by magnetic measurements on native and transplanted lichens from area subjected to arsons in Rome, Italy

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Keywords: Air pollution, Environmental magnetism, Magnetic properties.

Several areas of the city of Rome are frequently characterized by fraudulent fires, consequently arousing citizens' concern. We present a pilot study mainly based on magnetic measurement on native and transplanted lichens from two selected areas, in the eastern district of Rome, where fraudulent fires were set to recover metals, mostly copper, from WEEE (Waste electrical and electronic equipment). Both native and transplanted lichens have been sampled for magnetic susceptibility and hysteresis properties measurements. The results reveal intense and basically uniform magnetic properties connected to the complex anthropic context, where industrial, traffic and arson-related dusts are continuously emitted and bio-accumulated. Magnetic results have been correlated with those obtained from contaminants (e.g. heavy metals) analytical analyses carried out on the same samples. Significant positive correlations between the concentration dependent magnetic parameters (susceptibility, saturation magnetization and saturation remanence) and the concentration of heavy metals (among which copper, chrome, lead and zinc) have been highlighted. Moreover, selected individual magnetic particles have been chemically and morphologically characterized by using a Scanning Electron Microscope equipped with backscattered electron detector and Energy Dispersion System microanalyses. The particles are mainly incorporated in the lichens' tissues and the characteristic composition, morphology and grain size strongly support their anthropogenic origin. This pilot study confirms that the magnetic biomonitoring of lichens, combined with microtextural-compositional analyses, is an excellent multidisciplinary method to characterized environmental pollution in complex manmade areas.

# Chemical and mineralogical characterization of bottom ashes from a municipal solid waste incinerator in northern Italy, aimed at inertization and reuse

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Keywords: MSWI plant, bottom ashes, characterization.

Bottom ash is the solid residue produced by municipal solid waste incineration facilities, mainly made by unburnable and inert materials, and it represents about 20% in weight of the material treated by the incinerators in Europe. It is classified by the European Waste Catalogue as industrial non-hazardous waste, and its reuse is a common practice in many countries of Europe. Most of the bottom ashes from MSWI (municipal solid waste incinerators), depending on the legislation provided for each Country, is recycled as base material for landfill, for the production of cements and aggregates for civil infrastructures.

In Italy, around 82% of bottom ash produced by incinerators was treated in 2013 for reuse: most of the recovered material is represented by additive for cement (97%) and the remaining is destined to metal recovery (ferrous and not ferrous metals). According to the Italian Legislation about reuse of waste (Decree n. 186 of 5<sup>th</sup> April 2006) bottom ashes can be reused without any treatment or acceptance test for the production of cement, bricks and expanded clay. Heavy metals release and the high content of chloride and sulfate ions are the main factor that limit the reuse of bottom ash as secondary material, as in the case of road materials or cements.

The aim of this study is the characterization of the bottom ash coming from the Incinerator plant of the city of Turin, in northern Italy, to analyze its composition, and the leaching behavior, especially of heavy metals, in order to improve the reuse of it and to study possible ways of inertization. Different methods were applied to determine the chemical composition in function of the grain size of the material, as X-ray fluorescence, microwave digestion with ICP/OES analysis (EPA method 3051 A), SEM coupled with EDS probe, thermogravimetric analysis, mineralogical composition using X-ray diffraction. In general, bottom ashes exhibit a relevant dependence on particle size as to Si, Ca and heavy metals concentrations. Si decreases upon decreasing grain size, whereas Ca exhibits a reverse trend. Heavy metals tend to occur mainly in small size particles. In every particle size class is detected a phase composition characterized by a relevant occurrence of an amorphous phase (>70 wt%), along with minor phases as quartz, calcite and feldspar. Even the composition of the amorphous phase, calculated by subtracting the molar composition of the main crystalline phases, shows a dependence on the grain size, leading to different exchange properties in water. Leaching tests in deionized water (EN-12457) were also applied to each grain size of the material to compare the different behavior in water.

The results of such tests, combined with the determination on the solid phase, allowed to determine a different behavior of the material, depending on the grain size, with different features, and consequently different needs of treatment to reuse.

### Dispersion of Cu and Zn in terrestrial and marine systems: impact on environmental quality and aquatic life

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Keywords: mine, metal dispersion, precipitates.

Metals are a persisting threat to the environment. Metal toxicity largely depends on their speciation, as the more soluble forms are the more toxic. Toxicity is directly correlated to the concept of bioavailability, defined as is the degree of activity or amount of a pollutant available for activity in human or other organisms (Brown & Calas, 2011). Among metals, Cu and Zn are stable in solution under a wide range of pH, and so could become problematic for biota. These elements can reach important concentrations in some geologic frameworks, becoming a threat for the surrounding ecosystems. This is the case of the abandoned Libiola mine, where acidic water with a high load of Cu and Zn are directly discharged in the main watercourse of the area (Consani et al., 2017). As a result, the sudden precipitation and flocculation on the stream bed of an amorphous phase takes place. In this work, precipitates collected inside the mining area, in the torrent, and marine superficial bottom sediments were sampled in order to evaluate the dispersion and the mobility of Cu and Zn and observe the effects of metals on freshwater (diatoms) and marine (fishes) organisms.

The precipitates of the mining area are effectively able to retain Cu and Zn in the solid phase, with goethite better than schwertmannite, but the concentration of these elements are relatively low (2812 and 297 mg kg<sup>-1</sup> for Cu and Zn, respectively). On the contrary, the amorphous precipitates of the torrent are rich in Cu (up to 5.2 wt%) and Zn (up to 0.9 wt%), and an important fraction of these metals has been found to be mobile. This phase is the most important for the environment, as it controls the dispersion of metals outside the mining area. Marine sediments collected in front of the mouth of the torrent are richer in Cu and Zn (mean of 309 and 165 mg kg<sup>-1</sup>, respectively) compared to the other sediments of the area (41 and 70 mg kg<sup>-1</sup>, respectively). This difference in the concentration, due to the presence of coatings of amorphous Fe oxyhydroxides transported by the torrent, reflects also a different mobility, which is higher in the sediments near the mouth.

The detrimental effect of Cu and Zn on biota is observed on the diatom community of the torrent and on marine fishes. In fact, a shift of dominance to more tolerant and opportunistic species and many different teratological forms are observed in the diatom community downstream the mining area, whereas the effect of Cu and Zn can be observed in some fish tissues of specimen fished in the area.

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### Glassy wastes as feldspar substitutes in porcelain stoneware bodies: effect on sintering behavior

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Keywords: glassy wastes, feldspars, porcelain stoneware.

The production of ceramic tiles is continuously increasing worldwide, with a growing demand for raw materials: the challenge is to turn ceramic manufacturing sustainable in the long run, towards the transition to a Circular Economy. Although the use of residues is already entered in the industrial practice, its actual application in the ceramic manufacture is at present quite limited. The use of glassy wastes is usually hindered by technological reasons and kept to a few percent in a porcelain stoneware batch. As a matter of fact, a low-melting glass can significantly affect the firing behavior and particularly high temperature permanent deformations, the so-called pyroplasticity. Besides a general convergence towards a "fluxing effect" of waste glasses, it is not yet clear what is their influence on phase composition, composition and physical properties of vitreous phase, and eventually the sintering mechanisms and kinetics. The main goal of the present study is to assess the firing behavior of porcelain stoneware bodies containing glassy wastes. Six different wastes (bottles, PC-TV screens, lamps, glaze manufacturing, ceramic tile processing and grinding) - to a large extent glassy in nature - were added separately in increasing amounts, 20-40-60%, to a reference body up to a complete substitution of feldspathic fluxes (60%). The quantitative XRPD analyses (by Rietveld method) revealed that additions up to 40% keep the amount of liquid phase close to classic porcelain stoneware (60-75%). Nevertheless, an improved sintering kinetics was observed with lower temperatures of maximum densification (1060-1080°C vs. 1190-1220°C). The liquid phases existing at relatively low temperatures have a peculiar composition, due to both the waste glasses and the strong dissolution of mullite and quartz, but the relative stability of feldspars. The quartz present in the fired bodies (7-11%) is much less than in the reference body (22%). This implies a loss of solid load that could be ascribed for a permanent deformation of the ceramic slab. On the other hand, melting of quartz increases the silica content in the liquid phase; silica, being a glass network former, increases in turn the viscosity of the melt. An opposite mechanism characterizes feldspars. These two antagonistic phenomena determine the equilibrium between feldspars and quartz - i.e., the solid load - and the melt: a decreasing viscosity of the ceramic body (caused by crystalline phase dissolution) can be damped by a viscosity boosting of the liquid phase (for enrichment in lattice formers) or fostered by a viscosity drop due to feldspar melting. Therefore, the improvement of the sintering behaviour induced by the introduction of glassy wastes could allow the manufacture of large slabs in fast firing cycles, but it will be of the main importance to be able to predict the crystals-melt equilibria at high temperature to avoid phenomena of pyroplasticity.

# The High Performance Solidification/Stabilization process: a case study of Pb immobilization through recycling of contaminated soil

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Keywords: solidification/stabilization, heavy metals, recycling.

The approach to the reclamation of contaminated land is often realised with expensive techniques, which can generate huge quantities of wastes. From the end-of-waste perspective, as required by the Waste Framework Directive (Directive 2008/98/EC, 2008), it is necessary to develop techniques able to facilitate recycling, for providing both environmental protection and economic benefits.

The High Performance Solidification/Stabilization (HPSS) process is an eco-improved technology for treating contaminated soils, which has been recently engineered and applied to several large remediated sites, including the case study reported. The HPSS process follows the principles of traditional solidification/ stabilization (S/S) techniques, which aim at converting a toxic waste to a physically and chemically more stable form, involving chemical interactions between waste and a binding agent (Chen et al., 2009), usually Portland cement. In addition to that, the innovation supplied by the HPSS process derives by the use of superplasticizing and hydrophobizing additives and by including a granulation step at the end of the process, which result in the production of cementitious granular materials (i.e. pellets) (Ferrari et al., 2010). These pellets, characterized by low porosity and reduced leaching, could be reused as filling materials directly in the reclaimed area, to prevent waste production and new soil consumption.

The case study reported deals with the application of the HPSS process for the remediation of a former agriculture supply cooperative of the beginning of the XX<sup>th</sup> century, located in Bagnolo Mella (BS, Italy). The past activity of sulfuric acid manufacture, which was settled there and stopped during the eighties, now results in heavy metals contamination of soil. Pb is posing special concerns for its high concentration and mobility, the latter enhanced in the alkaline conditions induced by the binder. This study aims at investigate at the molecular and microstructural level the immobilization mechanisms controlling the retention of Pb, using advanced techniques as XAS, in addition to routine techniques as XRD, SEM/EDS and leaching tests. Additional strategies and improvements of the HPSS process, developed for solving problems related to the immobilization of amphoteric elements as Pb, are also presented.

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#### Karstic bauxite as low cost fluoride absorbent

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Keywords: Bauxite, Fluoride, low cost absorption.

Fluoride is one of the hazardous geogenic contaminant. In fact, despite F concentrations less than 1 mg/L are beneficial for calcification of dental enamel and bone formation, excess intake would lead to various diseases. Fluoride-related health disease are a common issue in the Eastern Rift Valley where, the high concentration of F in soils and drinking waters is related to the alkaline volcanic activity of the Rift Valley. Taking into account this important issue, many fluoride removal methods have been developed. Probably, the most popular remedy consists in treating waters with bone char. Today many processes like ion exchange, precipitation, coagulation, membrane processes, distillation and electrolysis are used as absorption. Among these, absorption is one of the most used method and involves passage of water through an absorbent material where F is removed by ion exchange or surface chemical reaction with the solid. Most of the available defluoridation materials are expensive or technically non-feasible for rural areas. Hence, F removal studies using i) low-cost, ii) locally available, iii) safe and iv) easy to use materials is of basic importance. Among the natural locally available materials, this study focuses on bauxite. Bauxite is a rock of large availability and exploited (e.g. Lushoto district) in central Africa. Aim of the research is to examine the potential of bauxite F removal from waters, analyzing the effect of various factors that control the removal (flow rate, contact time, particle size, co-existing ions, adsorbent dose, pH, initial fluoride concentration...).

Dynamic tests have been carried out using ppl columns with glass wool at the bottom (in order to prevent obstructions and avoid turbidity in the outgoing solution). An adjustable valve was placed in the bottom to control the flow rate. Working synthetic solution was prepared with NaF in order to obtain solutions at different concentration. The effluent was sampled each 25 ml. F dosage eluate was performed after pre-dilution with TISAB to reduce the ionic strength variation in the solutions.

Preliminary data highlighted that the uptake capacity increase with the contact time. As for the grain size, 0.2-0.5 mm class provided better results: finer classes restricted the solution flow whereas larger classes provided less contact surface.

The adsorption capacity was evaluated as mg of F removed per g of bauxite (Q value). In this way the maximum value obtained was higher than 0.10 mg/g. A second test using bauxite previously activated with  $H_2SO_4$  0.4 N was able to increase Q value up to >1 mg/g.

Concluding, these preliminary data suggest that bauxite may be used as a low-cost adsorbent for F removal especially in districts close to the ore deposits.

### 3-Years effects of zeolitite amendment practice on nitrate leaching from an agricultural soil located in a Nitrate Vulnerable Zone (Ferrara Province, Italy)

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Keywords: zeolitites, nitrate pollution, sustainable agriculture.

Negative impacts of agricultural activities on the environment are one of the most urgent problems to mitigate in order to guarantee a sustainable development. Nitrogen (N) losses following chemical fertilizer application is the main cause of the very low plant N use efficiency, worldwide. It is roughly estimated that more than 50 % of the N applied through fertilizers is lost in the environment. For these reasons, there is an urgent need to find and develop new methodologies that can help mitigating N losses and increase fertilizer use efficiency.

In this work we present an overview of the main outcomes of a 3-years experimental cultivation carried out in an Italian reclaimed agricultural field amended with different types of zeolities (rock containing > 50 % of zeolites), under cereals cultivation (*Sorghum vulgare Pers, Zea mays* and *Triticum durum*). The field is located in a Nitrate Vulnerable Zone (NVZ) and subjected to limitations on the maximum amounts of N applicable through fertilization. The aim of the experiment was to improve the soil physical-chemical characteristics by adding different types of zeolities as soil amendment. Zeolite properties (e.g. cation exchange capacity, affinity for NH<sub>4</sub><sup>+</sup> and reversible dehydration) influence the soil N cycle allowing to increase NH<sub>4</sub><sup>+</sup> retention (thus delaying nitrification processes) and consequently reducing NO<sub>3</sub><sup>-</sup> in waters discharged by the sub-surface drainage system (SSDS) of the field into the surface water bodies. Zeolitites were tested both in their natural state and in a NH<sub>4</sub><sup>+</sup>-enriched form, obtained through an enrichment process with NH<sub>4</sub><sup>+</sup> -rich zoo-technical effluents (pig slurry). The experimentation was performed reducing concomitantly chemical fertilizers application up to 50 %. NO<sub>3</sub><sup>-</sup> content in soils and in waters discharged through SSDS were periodically monitored during the whole experimental period and crop yield quantified.

Results showed that, for three consecutive cultivation cycles, the overall  $NO_3^-$  concentrations in water extracts was reduced by 45 % in the zeolitite treated soils, and by 64% in SSDS waters. Notwithstanding the lower N input from chemical fertilizers, crop yield was not negatively affected by the zeolitite amendment and increased up to 21 % with respect to the controls. Zeolitite addition thus enhanced soil  $NH_4^+$  retention, reducing also  $NH_3$  volatilization (see Ferretti et al. (2017)), allowing a better fertilizer use efficiency by plants and a reduction of the overall  $NO_3^-$  concentrations in the surface waters.

Ferretti, G., Keiblinger, KM., Zimmermann, M., Di Giuseppe, D., Faccini, B., Colombani, N., Mentler, A., Zechmeister-Boltenstern, S., Coltorti, M. & Mastrocicco, M. (2017): High resolution short term investigation of soil CO<sub>2</sub>, N<sub>2</sub>O, NO<sub>x</sub> and NH<sub>3</sub> emissions after different chabazite zeolite amendments. Appl Soil Ecol., 119, 138-144.

# Short-Term response of soil microbial biomass and gaseous emissions to different chabazite zeolitite amendments

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Keywords: zeolitites, soil microbial biomass, gaseous emissions.

Zeolitites (ZTs) are rocks containing more than 50 % of zeolites and are worldwide recognized as a suitable and valuable soil amendment.

Once homogenized in the soil or in the cultivation substrate, ZTs enhance soil physicochemical properties and nitrogen (N) use efficiency. However, little is known about their effects on soil microbial biomass and on how they influence soil gaseous emissions, which may represent an important contribution of greenhouse effect.

This study aims at i) evaluating short-term effects of different chabazite-rich ZT (CHAZT) amendments on soil microbial biomass and activity and ii) evaluating the effects of different CHAZT amendments on soil gaseous emissions (CO<sub>2</sub>, N<sub>2</sub>O, NO<sub>x</sub> and NH<sub>3</sub>) soon after the application.

To reach these goals a silty-clay agricultural soil was amended with different percentages of natural CHAZT (NZ, at 5 and 15 wt%) and NH<sub>4</sub>-enriched CHAZT (CZ, at 10 wt%) in two separate incubation experiments.

In the first incubation experiment, soil dissolved organic carbon (C), total dissolved N, NH<sub>4</sub>, NO<sub>3</sub>, NO<sub>2</sub>, microbial biomass C and N, and ergosterol were measured periodically over a 16 day period. To verify the microbial immobilization of the N derived from CZ, a naturally high <sup>15</sup>N source (pig slurry) was used for enriching the mineral and microbial biomass <sup>15</sup>N signature was monitored over the incubation.

In the second incubation experiment, an investigation of soil  $CO_2$ ,  $N_2O$ ,  $NO_x$  and  $NH_3$  fluxes was carried out for a total of 24 h both immediately after the application of urea and without a further N input.

Concerning the effect on soil microbial biomass (first experiment), ergosterol content increased in the soil amended with 5 % NZ while no clear trends were observed in the soil amended with 15 % NZ, suggesting that fungal biomass was favored at lower application rate. CZ amended soil showed evidence of nitrification, since microbial biomass N was directly related to NO<sub>3</sub> production and inversely related to NH<sub>4</sub>. Isotopic measurements confirmed immediate assimilation of N derived from CZ.

In the second experiment, immediate  $CO_2$ ,  $N_2O$ ,  $NO_x$  and especially NH<sub>3</sub> emissions after fertilizer application were generally reduced (up to 60 %) in soils amended with NZ, indicating it as a valuable material for reducing soil C-N gaseous losses. CZ application lowered  $CO_2$  and  $N_2O$  emissions, but very high  $NO_x$  fluxes occurred even without applying any further N input. NH<sub>3</sub> emissions were higher in NH<sub>4</sub>-enriched zeolites amended soil, but if the amendment is performed without further N inputs, the emissions can be significantly lowered with respect to a conventional urea fertilization.

These results suggested that the CZ used in this study supplied an immediately available N pool to the microbial biomass and that NZ can be a suitable material for mitigating gaseous N and C losses from soil or substrates.

#### Bioleaching of alkaline wastes using mixed bacterial culture sourced from a natural system

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Keywords: MSWI solid residues, Steel slag, Metal removal.

Establishing an efficient technology that fulfils environmental and industrial requirements is of paramount importance to foster a circular economy, as advocated by the European Commission. We present an ecofriendly and cost-effective biotechnology for the treatment of two types of alkaline wastes, such as municipal solid waste incineration (MSWI) ashes and slag from steel making industry. Both contain many hazardous metals as well as other elements that may be worth recovering. The existing technologies for the treatment of these waste materials are inadequate for extracting secondary raw material or safe disposal. The method development is the key objective of the present work to provide industrial managers with a reproducible and scalable solution. Our main tasks include: (1) cultivation and adaption a mixed acidophilic bacterial community collected from a natural system to the different waste substrates; (2) assessing the bioleaching of metals from the selected residues; (3) assessing the metal recovery using ion exchange resins. The leaching of metals from the bulk materials was investigated in a controlled lab environment using a natural mixed culture where Acidothiobacillus thiooxidans and Acidothiobacillus ferrooxidans are the dominant strains. The bio-assisted leaching provided good yields of metal extraction exploiting the bacterial catalytic production of sulphuric acid. We assessed different experimental setups, and a comparison between two different regenerating ionexchange resins is provided. The potentially recoverable metals and the environmental stability of the final residues will be discussed.

### Mineralogical characterization of MSWI bottom ash

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Keywords: MSWI plant, bottom ashes, characterization.

The incineration process reduces the mass of input waste by up to about 70 % producing complex inorganic materials called bottom ashes. Due to different type of waste burned (input), temperature inside the combustion chamber, reaction conditions, and chemical additives the final material (output) is very heterogeneous and mainly composed of fine-grained particles, melt and metallic components, synthetic materials, as well as unburned organic matter (Chimenos et al., 1997). Heavy metals are incorporated into glassy phases or wellformed minerals that may undergo mineralogical changes when exposed to the atmosphere or subjected to treatment processes. Bottom ashes sampled from Parma WTE plant were chemically and mineralogically characterized by means of XRF, ICP-MS, XRD, optical microscopy and SEM-EDS. XRD patterns of BA show a large quantity of amorphous phases (about 70 wt%) and mineral phases including silicates, cementlike phases, carbonates, and spinels. Due to the large amount of amorphous material a well-detailed SEM-EDS could be a good method to investigate from a morphological and chemical point of view, thin sections composed of clasts of different dimension. Bottom ashes consist mainly of a Si-Ca-Al-O vitreous matrix in which some crystalline fractions are embedded. The vitreous matrix contains streaked flow structures and tiny circular vesicles formed by degassing. Inside this matrix, dendritic forms and few idiomorphic crystals range from 1 to 50  $\mu$ m in diameter and show a composition along the solid solutions akermanite-gehlenite, indicating that new mineral phases during the incineration processes and the subsequent quench were formed. Single large crystals of quartz, pyroxenes, and feldspars are frequently observed as well as ceramic fragments and concrete. The latter are clearly identifiable probably because they passed through the incineration process without significant changes in their mineralogy and chemistry (refractory materials). Fine lamellae probably formed during cooling of the phases together with rounded shapes of the dendrites have been found within the spinel crystals as a result of a reaction with the melt. The chemical composition of the spinels is often represented by Fe, Ti, Mn with a dimension of few microns. Metal inclusion, zonation, and dissolution structures were observed by using back-scattered micrographs. These mineralogical features frequently show a Ti- or Mn-rich core and a Fe-rich rim, suggesting that the crystallization processes ceased in a condition of thermodynamic disequilibrium. Several analyses are still underway to define in which crystalline or amorphous structures other heavy metals are located.

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# Chemical SEM-EDS maps and cathodoluminescence analyses as a possible method to characterize bottom ash

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Keywords: Bottom ash, SEM-EDS, cathodoluminescence.

Despite the widespread use of recycling in Italy, approximately 30% of all waste produced is burned producing energy for electricity and heating system and ash, re-used in civil engineering works (roads, earthworks, backfill, etc.). Currently the Italian regulation on waste-to-energy plants (D.lgs. 152/2006 - 2008/98/CE) classifies bottom ashes as non-hazardous waste but studies on the effective ecotoxicology are still ongoing especially after the new regulation EU 997/2017.

Bottom ashes are an extremely heterogeneous material, in terms both of composition and morphology: they consist mainly of a Si-Ca-Al-O vitreous matrix in which some crystalline fractions are embedded.

Inside amorphous material as well as in crystals potentially toxic elements may be included: the specific hazard depends mainly on the metal-containing structures that may release this element over time and in a subsequent reuse (Wei et al., 2011).

Many works investigate BA through MO, SEM-EDS, XRD but due to the heterogeneity and complexity of the material, the characterization is often carried out on a macro scale, and only very few works on micro scale (Speiser et al. 2001). Polished thin sections from little clast taken randomly in the bottom ash were examined by cathodoluminescence (CT) mounted on an optical microscope and analysed by electron probe microanalysis. X-ray mapping of the trace elements were also performed on the same thin section. The interpretation of the obtained data from these different analytical methods provides useful information on the chemical zoning of the streaked flow structures found in the ash. Amorphous areas represented by a Si-Ca-O vitreous matrix show a complex CT, consisting of large red-pink and blue bands. Inside this vitreous matrix dendritic structures and fine lamellae with a CT colour pale blue are present. Combining chemical maps from EDS and CT images a correlation between the concentrations of some element (mainly Al, Mn and Fe in the pseudo-wollastonite structure) and the CT blue-pink emission are found. Instead, the pale blue CT emission is probably connected with non-compositionally controlled lattice defects. More detailed analyses are in progress but this early stage study shows a good potential method to characterize a very complex mineralogical assemblage.

Wei, Y., Shimaoka, T., Saffarzadeh, A., & Takahashi, F. (2011): Alteration of municipal solid waste incineration bottom ash focusing on the evolution of iron-rich constituents. Waste management. 31, 1992-2000.

Speiser, C., Baumann, T., & Niessner, R. (2001): Characterization of municipal solid waste incineration (MSWI) bottom ash by scanning electron microscopy and quantitative energy dispersive X-ray microanalysis (SEM/EDX). Fresenius' Journal of Analytical Chemistry, 370, 752-759.

### Reconstruction of geomorphic dynamics in slope affected by water driven processes: geopedological approach to two study cases in the western italian Alps

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Keywords: soil, paleosols, water driven processes, gully systems.

In mountain environments, soils may play a key role in the reconstruction of the evolution and dynamics of slopes affected by water driven processes. In fact, soil formation and evolution are closely linked to environmental parameters as relief, time, parent material, climate and organic activity (Jenny, 1941). Moreover, the soil could also be important for its function as archive; like the other paleo-environmental archives, it contains accurate information over large time intervals on continental Quaternary variations.

The main aim of this study is to reconstruct the evolution of slopes, by means of a geopedological approach, in two areas in the Western Italian Alps (Saint Nicolas, Aosta Valley; Gran Gorgia, Susa Valley) affected by the presence of gully systems locally characterized, along their flanks, by the development of pseudo-badlands features.

In both the study areas, selected soil profiles were excavated along slopes for investigating the slope dynamics, on the edge of the badlands in order to understand the dynamics of soil erosion due to the action of water driven processes, and, finally, in a flat and stable area for analyzing soil development in a more stable geomorphological context.

Soil profile analyses took advantage of multiple laboratory techniques (i.e., particles size distribution, C organic content, total N content, pH, Al and Fe oxides content, Rock-Eval pyrolysis) providing a more complete reconstruction of the slope evolution.

In both the study sites, soil profiles located along slopes and at the badlands edges are characterized by a weakly degree of development, probably caused by the continuous sedimentation/erosion phases due to colluvial events and water driven processes. Instead, the soil profiles located in stable and flat areas show a good degree of development. Anyway, some differences have been detected between the two sites. Only in Saint Nicolas study area the soil had recorded the occurrence of colluvial events; indeed, only in this site the alternation of aggradation/degradation episodes along the slopes are supported by the presence of buried surface underlined by the occurrence of grain-size discontinuity and of a peak of organic Carbon content. Whereas, in the Gran Gorgia study site no buried surfaces have been detected.

Finally, also the human presence is not negligible in these two areas and it may influence the presence and the magnitude of geomorphological processes.

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### The role of Chromite Ore Processing Residue (COPR) in groundwater pollution: The Ex-Stoppani site (Arenzano, Genova Italy)

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Keywords: COPR, Chromium, Selective Extraction.

Chromite ore processing residue (COPR) is a high pH waste containing elevated residual total Chromium concentrations a part of which occur as Hexavalent Chromium ( $Cr^{VI}$ ) (10 to 30wt%) (Chrysochoou et al., 2010).  $Cr^{VI}$  is carcinogenic when inhaled or ingested with drinking water; the World Health Organization (WHO) fixed a guideline value of 0.05 mg l<sup>-1</sup> for total Cr in drinking water(WHO 2011). The Stoppani S.p.A. industry located in Arenzano (Genova, Italy) since 1901 until 2003, transformed Cr<sup>III</sup> from chromite mineral (FeCr<sub>2</sub>O<sub>4</sub>) to Cr<sup>VI</sup> based products such as sodium dichromate, chromic acid and basic chromium sulphate.

The uncontrolled discharge of millions of tons of COPRs in all the area caused severe problems of soils contamination and release of high quantities of Cr<sup>VI</sup> in percolating water.

Mineralogical characterisation of COPR samples, performed by X-Ray powder diffraction (XRPD), Micro-Raman Spectroscopy and Scanning Electron Microscopy showed the typical mineralogic composition of COPRs:relicts of un-reacted Chromite;Brownmillerite and Larnite high-temperature phases;Calcite, Dolomite, Gypsum, Ettringite, Brucite weathering phases;also Sodium Chromate and Crocoite were detected.

To evaluate and quantify the mineralogical control on Cr<sup>VI</sup> release the first step of Community Bureau of Reference (BCR) selective extraction procedure (Quevauviller, 1998) is applied and compared with extraction by de-ionised water. Therefore, two different aliquots of COPRs were treated with de-ionised water and with 0.11M acetic acid (CH<sub>3</sub>COOH) to extract water-soluble and exchangeable/acid-extractable, respectively. Leachates were analysed by ICP-OES and ICP-MS for major, minor and trace element composition. Cr<sup>VI</sup> concentration was determined using 1,5 dyphenilcarbazide colourimetric method (Petala et al., 2013).

High concentrations of  $Cr^{VI}$  (0.40 - ~400 mg l<sup>-1</sup>), depending on sample nature (i.e. COPR or roasting materials), are extracted by de-ionised water, while results of extraction in acetic acid are more challenging to be interpreted.

Results of different analytical methods will be compared and discussed to identify soluble mineral phases releasing Cr<sup>VI</sup> in percolating water.

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### Chromite Ore Processing Residues (COPRs): Mineralogical characterisation, the case of Ex-Stoppani site (Arenzano, Genova Italy)

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Keywords: COPR, Mineralogical Composition, CrVI release.

Toxic metal pollution has become a severe problem in industrialisation process at regional scale. Among the toxic metals, Hexavalent Chromium ( $Cr^{VI}$ ) is a Class A carcinogenic, D.M. 14/2016 fixed its limit at 10 ug I<sup>-1</sup> in groundwater. The over 100 years of production of Sodium Chromate, Chromic acid and Basic Chromium Sulphate in the Ex-Stoppani area (Arenzano, Genova Italy) via high lime process, transformed CrIII from chromite mineral (FeCr<sub>2</sub>O<sub>4</sub>) to Cr<sup>VI</sup>. Discharge of millions of tons of Chromite Ore processing Residue (COPR) in all the area caused severe problems of groundwater contamination, being Cr<sup>VI</sup> very soluble and mobile. For these reasons, an accurate characterisation of COPRs is necessary to deepen processes controlling retention and release of Cr<sup>VI</sup>.

COPRs present a very complex mineralogical composition, so a complete mineralogical and minerochemical characterisation require a multi-technique approach: X-Ray Powder diffraction (XRPD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX) on thin and dry polishing sections and Micro-Raman Spectroscopy on the untreated sample.

Mineralogy of studied samples can be rationalized in three main categories: residual roasting chromite of composition Magnesium Chromite  $(MgCr_2O_4)$  - Chromite  $(FeCr_2O_4)$  solid solution at core and Magnesium-Ferrite  $(MgFe_2O_4)$  - Spinel  $(MgAl_2O_4)$  at rim; COPR mineral phases generated during roasting process: Brownmillerite  $(Ca_2(Al,Fe^{3+})_2O_5)$ , Larnite  $(Ca_2SiO_4)$  and many hydration products such as Brucite  $(Mg(OH)_2)$ , Katoite  $(Ca_3Al_2(OH)_{12})$ , Gypsum  $(CaSO_4 \cdot 2(H_2O))$  Calcite  $(CaCO_3)$  and Ettringite  $(Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26(H_2O))$ ; soil mineral phases derived by mixing with other materials: Quartz  $(SiO_2)$ , Muscovite  $((K,Na)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2)$ , Albite  $((Na,Ca)Al(Si,Al)_3O_8)$  and clinochlore  $((Mg,Fe^{+2})_5Al(Si_3Al)O_{10}(OH)_8)$ .

It is noteworthy that micro-Raman analysis of untreated COPR also revealed the presence of Crocoite (PbCrO<sub>4</sub>).

Deepen knowledge of COPR mineralogy and identification of Cr-bearing mineral phases involved in specific reactions of retention and release of CrVI in groundwater is furthermore necessary for any remediation action.

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#### Monitoring soil organic matter content in croplands through Vis-NIR-SWIR spectroscopy

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#### Keywords: Spectroscopy, topsoil, Organic matter.

Organic matter has an important role in the chemical, physical and biological processes occurring in the soil, since it provides nutrient supplying, pH buffering, increasing water-holding capacity, improving soil structure and porosity, limiting of erosion and compaction, reducing surface crusting, degrading and filtering pollutants, and sustaining soil biodiversity. Increasing soil organic matter (SOM) generally results in increasing soil productivity and reducing the atmospheric  $CO_2$  content that contributes to climate change. In addition, the preservation and restoring of SOM through appropriate land uses and soil management are fundamental for the landscape and biodiversity protection.

In hilly landscapes, erosion is responsible of SOM depletion in topsoils. Tillage erosion has been recognized as one of the main erosive processes affecting croplands in hilly terrains. It involves the displacement of the cultivation layer and is primarily due to mechanical implements. Topographical parameters also control the extent and severity of tillage erosion. Tillage erosion can be evidenced from differences in soil properties along a hill slope (van Oost et al., 2006). Intensive tillage erosion results in substantial soil truncation and within field redistribution of soil. Continuing removal of topsoil and the subsequent lowering of the plough layer on convexities lead to the incorporation of SOM-depleted subsoil material in the plough layer. At the same time, tillage accumulates soil at concavities where a deep soil enriched in organic matter develops.

Due to the large variability of SOM in the 3D space, the mapping of SOM spatial distribution with traditional techniques is very difficult (Costantini and Dazzi, 2013; and references therein).

VIS-NIR spectroscopy has been successfully used for estimating the SOM content of topsoils (Conforti et al., 2013), although many variables affect the spectral fingerprint of SOM in soil, such as texture, structure, moisture, and mineralogy. The present research is the continuation of a previous study, where field- or farm-scale calibration of VIS-NIR and SWIR spectroscopy with standard soil analyses have demonstrated to be promising in estimating SOM abundance. Here we attempt to extend our investigation to evaluate the influence of other variables, including soil management, on SOM predictions.

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# Role of weathering of pillow basalt, pyroclastic input and geomorphic processes on the genesis of the Monte Cerviero upland soils (Calabria, Italy)

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Keywords: pillow basalts, weathering, soil genesis.

The knowledge of weathering and soil formation processes on pillow basaltic rocks in the mountainous environments of the central Mediterranean area is quite poor. We present new data on weathering and soil formation processes involving alkaline pillow basalts intruded in a Meso-Cenozoic carbonatic sequence, outcropping on the Mt. Cerviero (Calabria, southern Italy). We investigated two different soil profiles using a multidisciplinary approach, including macro/micromorphological and chemico-physical pedological investigations, as well as petrographic, mineralogical and geochemical analyses. These analyses permitted us to distinguish the main features related to the hydrothermal alteration of the pillow basalts in a submarine environment from the chemical weathering processes affecting the primary minerals in the bedrock under meteoric conditions. The radial weathering pattern of the bedrock appears controlled by the subspherical shape of the pillows and the outer concentric rims, affected by surface cracking, flaking and illuviation of Fe-Mn oxides and clay coatings. Irregular geochemical patterns shown by ratios between pairs of several major and/ or trace elements and CIA values across the soil profiles and the pedological analyses indicate a lithological discontinuity between the bedrock and the topsoil horizons, which suggest a rejuvenation of the pedogenetic front, due to colluvial and erosive processes and allochthonous pyroclastic input. In accord with this, the soil profiles display an overall poor to moderate degree of development, also indicated by the phyllosilicate clay mineralogy, despite the old ages of emplacement (Jurassic) and exhumation (Miocene) of the pillow basalts. Illuviation of clay and iron-manganese coatings in the Bt horizon of soil profile MC1 suggests an emplacement under warm-humid conditions probably during the last interglacial. The degeneration microtextures of the clay pedofeatures, caused by argilloturbation, bioturbation and/or cryoturbation processes, indicate their relict genesis. A Late Pleistocene to Holocene age of soil development is confirmed by the poor volcanic glass shards and vesiculated pumices of trachytic composition, identified using SEM-EDS in the topsoils of both profiles. These volcanic ash fragments can be related to the Late Pleistocene and Holocene eruptions from the Campania Province (Vesuvius and Campi Flegrei) or the Aeolian Islands (mainly Lipari and Volcano). Furthermore, the presence of volcanic glass together with the optically isotropic pedogenic matrix of the soils are consistent with the occurrence of some poorly-crystalline clay minerals, derived from the weathering of glass fragments, and with the Andosol-like field features of both the studied soil profiles, even if they developed in a non-volcanic area.

#### Bottom ashes as a sink for the anthropocene mineralogy

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Keywords: anthropocene, inicnerator, municipal soli waste.

A major human skill, and a sharp signature of what is now accepted as anthropocene, is the capability to differentiate. Relying just on synthetic phases we had a jump from the 5500 known minerals, to the 180000 potential synthetic anthropocenic new phases (Hazen et al. 2017). Whereas most geochemical investigations on Earth materials have the goal to ascertain the process of differentiation, we have also sinks, like mantle and sub-ducted crust. In anthropocene a sink is doubtlessly the incineration process.

During incineration, organic matter is mostly burned out, and the inorganic component is present mostly in bottom ashes, respectively 20 % of the original mass. Bottom ashes represent therefore a sampling of the human activity devoid of most organic chemistry compounds. Although heterogeneous in its composition and mineralogy, with significant differences in the grain size, sampling locality and season, analysis from incinerators from all over the world show striking similarities as long as an average composition is considered. To verify whether and how this composition deviates from the average natural source, we have examined the average composition of the bottom ashes obtained from 14 plant from different nations and assumingly with different waste input and disposal policies, and compared the results with those from the average continental crust rocks is strikingly different, owing to the different material provenance, and thermal history, but here it is assumed as a starting point that continental crust as a whole is the input for the inorganic materials of wastes.

The single plants show some significant difference, most in Si and Ca content, but on average, for major elements we found that the element distribution follows a trend which is predictable by average continental crust (R2=0.86, slope and intercept respectively 1.00(14) and -0.09(13) vs 1 and 0 expected in the ideal case of no change vs ACC). An exception is given by Si and Ca, which are for all the examined plants always lower and higher of the average continental crust, respectively. The values for Ca and Si are intermediate between those of the ACC and of Portland cement.

As concerns minor elements, we find an enrichment in several elements in MSWI, namely Cu, Cd, Sb, Zn, Pb, Cl, Zn, Mo, Sn, Bi, which are enriched by more than one order of magnitude respect to ACC. In general, bottom ashes are more metal enriched than continental crust. However, also in trace elements, the element composition is related to that of ACC (R2=0.56).

As a conclusion, elemental distribution patterns found in ACC are, as a whole, preserved also in bottom ashes. Signatures and exceptions in elemental distribution should be regarded carefully to verify the social and industrial behaviour and policies underlying the processes of waste disposal.

Hazen, R., Grew, E., Origlieri, M. & Downs, D. (2017): On the mineralogy of the "Anthropocene Epoch". Am. Mineralogist, 102, 595-611.

### Magnetic monitoring of PM at INGV: a summary of key results, perspectives and outreach activities

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Keywords: atmospheric pollution, magnetic properties, particulate matter.

INGV paleomagnetic laboratory has been involved for over 15 years in many research activities about the magnetic properties of atmospheric particulate matter (PM), ranging from biomonitoring studies on leaves and lichens to analyses on filters from air monitoring stations, as well as dusts emitted by cars.

The first surveys were addressed to the biomonitoring of PM in Rome, sampling *Platanus sp.* and *Q. ilex* leaves, proving that the concentration dependent magnetic parameters are excellent proxies of the long-term pollution loadings.

The next studies involved  $PM_{10}$  air filters, pointing out that the most of anthropogenic  $PM_{10}$  in Rome originates from motor vehicles.

Afterwards, magnetic and electron microscopy analyses were combined to discriminate the sources of different magnetic PM fractions; Fe-rich particles from disk brakes powders and from exhaust pipes were compared to those from leaves and air filters, which showed mixed contribution from all the sources.

Further analyses on the role of ultrafine superparamagnetic (SP) particles in the overall magnetic assemblage of traffic-related PM showed that the SP fraction mainly occurs in association to coarser multidomain magnetite-like grains.

The next research line was directed to lichens, both native and transplanted, sampled around a cement plant in Slovakia. The results pointed out the suitability of lichens as air pollution magnetic biomonitors, after considering the geological background that may affect their magnetic properties.

Transplanted lichens were also exposed for 2 months in a mixed land-use area in northeastern Italy. The post-exposure element content and the magnetic data are correlated and reveal a modest anthropogenic impact on the territory, mostly limited to an industrial park. The study confirmed that lichens are effective bioaccumulators and their magnetic properties are excellent proxies for heavy metal pollution. With a grid of lichen transplants it is possible to monitor the variations of their magnetic properties according to a known exposure period and initial conditions, with the possibility of covering unvegetated areas, thus bypassing the intrinsic limits of magnetic measurements on leaves.

The results of our research have often been presented during public outreach events; moreover, teams of secondary school students have conducted surveys of the magnetic properties of leaves in Rome, thus introducing rock-magnetism basics while raising awareness of urban environmental pollution.

Moreover, in 2017, these results have been shown to hundreds of students attending to an educational project organized with the Municipality of Rome.

This review aims to stimulate the integration of magnetic data on environmental pollution with technical, biological and medical aspects, to promote new perspectives and wide applications to this field of research.

### **Session S29**

## Environmental pollution related to occurrences of asbestos and asbestiform minerals in geo-matrices

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### In situ multi-analytical approach for Identifying asbestos minerals

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Keywords: chrysotile, asbestos tremolite, portable digital microscope.

Nowadays, due to the adverse health effects associated with asbestos exposure, various laboratory techniques are used to characterize the occurrence of asbestos fibers in rock samples. Although to date sporadic studies have been carried out on asbestos identification using portable devices (Roger et al., 1999; Petriglieri et al., 2017), in recent years both the portable XRF and portable Raman techniques have been successfully used for the chemical and mineralogical characterization of rocks and artifacts. The aim of our study is to promote the portable monitoring of asbestos fibers present in rock outcrops, using portable digital microscope (p-DM), portable X-ray fluorescence (p-XRF) and portable  $\mu$ -Raman spectroscopy (p- $\mu$ R). To achieve this ambitious goal, we cross-checked the data obtained from the p-DM, p-XRF and p- $\mu$ R on the serpentinites and metabasites outcropping in the Gimigliano-Mount Reventino Unit (GMRU) (Bloise et al., 2014). The portable digital microscope enables us to distinguish fibrous and other morphologies. Analysis with p-XRF is not sufficient to solve the issues regarding the identification of asbestos minerals, however it enables us to distinguish between serpentinitic and amphibole asbestos phases. Finally, the chrysotile and tremolite asbestos were easily identified due to their characteristic Raman spectrum. The asbestos minerals found in the outcrops analyzed are consistent with the findings of previous studies (Bloise et al., 2014). This study (Bloise & Miriello, 2018) highlights the versatility and effectiveness of portable micro-Raman Spectroscopy which enables us to obtain reliable information on the mineralogical distinction between different fibrous phases (i.e., chrysotile and tremolite). The authors are aware that conventional laboratory analyses must be carried out to obtain an accurate mineralogical characterization of outcropping minerals. However, the simultaneous use of portable analyzers (p-DM, p-XRF and p- $\mu$ R) may prove useful for: (i) the rapid identification of fibrous asbestos minerals especially when sampling is not possible (e.g., doorways of churches or columns with serpentinite rocks); (ii) developing a targeted sampling plan for identifying areas polluted with both asbestos minerals and heavy metals. Moreover, this approach can be preparatory for optimizing additional specific techniques aimed at classifying NOA.

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### Preliminary study of asbestos minerals in the area of Episcopia (Lucania, S-Italy)

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Keywords: Naturally Occurring Asbestos (NOA), Southern Italy, Mineralogical characterization.

Today, it is widely accepted in the scientific community that exposure to asbestos is associated with the development of damage to health. Among the minerals which form the airborne particulate, the most hazardous ones display a fibrous-asbestiform crystal habit. Naturally occurring asbestos (NOA) is a term referring to asbestos present in rocks and soils to distinguish them from asbestos contained in asbestos containing materials (ACM). The Lucania region (southern Italy) is characterized by wide occurrence of serpentinite rocks (Bloise et al., 2017), that are removed from their natural place of origin to be used as building which contain tremolite/ actinolite asbestos and/or chrysotile (Massaro et al., 2012). Owing to possible health problems due to asbestos fiber dispersion, these types of quarries are regulated by the Italian law (DM 14/06/1996) which demands the asbestos presence identification. A preliminary study to investigate on the presence and nature of asbestos mineral is carrying out on 12 natural rock samples collected in the ophiolites of the Frido Unit. Episcopia village is located to south-western of the thrust-top/piggyback of S. Arcangelo basin. The pre-pleistocene substrate (Episcopia-San Severino melange) is characterized by articulated overlapping of tectonic flakes belonging to different Units and Formations. Along the Sinni River the calcschists and phyllites to the Unit of Frido outcrps. On this Unit it often find lenticular metabasites interbedded with and highly fractured serpentinites. In a stratigraphically superior position Crete Nere and Saraceno formations and the Flysch of Albidona appear. These are non-metamorphic lithotypes referable to the North-Calabrian Unit.

The samples have been analyzed by X-ray powder diffraction (XRPD) and scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS). To do unambiguous identification of the serpentine varieties (i.e. chrysotile, lizardite, polygonal serpentine, antigorite), more precise characterization of each sample was performed by transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). Preliminary results have shown that serpentinite samples contain asbestos minerals such as chrysotile, tremolite, and actinolite with talc, willemseite, chlorite and clay minerals also detected in variable amount. The preliminary results of this study show that the occurrence of serpentinite rocks can have serious health impacts on the people residing in the surrounding area. The detection of asbestos minerals is essential from both to legislative and scientific point of view, especially for the administrative agencies whose task it is to safeguard public health and implement construction and safeguard policies.

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### X-ray tomographic microscopy study of serpentine veins in massive serpentinite

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Keywords: veins, serpentine infill, microtomography.

Serpentinization, a hydrothermal alteration of ultramafic rocks (e.g. peridotite, pyroxenite), mainly occurs in two geological settings on the Earth: i) ocean floor, mid-ocean ridges; ii) subduction zones. Serpentinization greatly modifies the physical, mechanical, and chemical properties of ultramafic rock, which can be partially or totally serpentinized. Serpentinization is accompanied by abundant veining marked by different generations of vein-filling serpentine, which induces a decrease in density. Serpentine veins in hydrated peridotite are particularly abundant and display a vast and complex variety of textures and morphologies. This variety reflects numerous mechanisms of vein formation and fluid conditions recorded by various serpentine mineral assemblages (Andréani et al., 2007). It is worth remembering that the dominant type of serpentine infill is the fibrous one (e.g. chrysotile, protoserpentine, polygonal serpentines). Vein infill typologies are conventionally studied by using optical and scanning electron microscopy (SEM), which only allow two-dimensional (2D) imaging of samples. In this work we present results obtained by the application of high-resolution X-ray computed microtomography which provided a realistic visualization of the 3D shapes and orientations of veins that can be quantified through the extraction of parameters such as volume fraction, size distributions, orientation and connectivity. Furthermore, the phase-contrast mode allowed to detect the crystals with chemical composition different from the serpentinite group minerals (e.g., magnetite). We have investigated the serpentine vein infill, which crosscuts massive serpentinite bodies cropping out in the Gimigliano-Mount Reventino Unit (Calabria, Southern-Italy) (Bloise et al., 2016). Obtained data allowed to evaluate i) the geometric interface between serpentine-fibrous infill veins and the matrix; ii) the percentage of serpentinization; iii) the percentage of fibrous minerals in massive serpentinite rocks.

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# Ophiolitic rocks of the Timpa delle Murge-Timpa Pietrasasso in the Pollino GeoPark (southern Italy)

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Keywords: Ophiolites, serpentinites, Pollino GeoparK, southern Italy.

The ophiolites represent a fragment of oceanic crust, with relative sedimentary cover, and are evidence of an ancient ocean basin known in geological literature as Western Tethys or Alpine Thetys (Stampfli et al., 2002). The rocks of the ophiolitic sequences are known as "green rocks" from the color of the most common lithotypes, the color is reminiscent of the skin of a snake. In the Pollino Geopark the ophiolitic rocks are the testimony of the Jurassic ocean floor in the Thetys realm. The ophiolitic rocks widely outcrop in natural environment and are well exposed in the Timpa delle Murge-Timpa Pietrasasso area. They consist of the the asbestos-bearing serpentinites and minor metagabbros, metabasalt, pillow lavas, diabase rocks and their sedimentary cover (radiolarites, limestones and shales) and are associated with shales, calcschists, metalimestones, and fragments of continental rocks (gneiss, amphibolite), which provide information about the geodynamic evolution of these rocks. The serpentinite rocks derive from serpentinization processes connected with the alteration of the olivine that have involved green-bluish mantle peridotites of Tethys oceanic basin. The reaction takes place for ocean floor metamorphism in the oceanic ridge, during ophiolites obduction processes (Barker, 1998).

The serpentinite rocks are rather unfavourable to the piant growth, even inhospitable in extreme cases, are really inhabited by a smaller number of species than other types of geological substrate.

The areas with serpentinite rocks have high priority for biodiversity conservation because of the relatively large numbers of endemic species and ecotypes. We are observed that both plants and animals on serpentinite show special qualities. Among the plant species is notes holly (Ilex Acquifolium) and different kinds of orchid (Dactylorhiza SPP. o Orchis SPP.) and siderite (Cerastium Tomentosum) used by pastor as medicament in the past and the presence of beetle (Rosalia Alpina). Among animal species reported in the Timpa delle Murge-Timpa Pietrasasso area reveal: the wolf (Canis Lupus), the black woodpecker (Dendrocopos Martius), the red kite (Milvus Milvus). Ophiolites of the Timpa delle Murge-Timpa Pietrasasso sequences has an important interest in geology, biology and history. The panorama section represent the important geosites in the Pollino GeoPark which provide important information for the paleogeographic reconstruction of the Mediterranean area. These geosites, UNESCO heritage, have been enhanced with the realization of educational-naturalistic trails and with explanatory panels for the conservation and dissemination of this important geological heritage.

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#### Natural Cr(VI) contamination of Tuscan serpentinite-hosted spring waters

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Keywords: Chromium, serpentine outcrops, carbonation.

Serpentinites, or metamorphosed ultramafic rocks, are distributed worldwide and contain Cr concentrations typically greater than 2000  $\mu$ g/g. Leaching of chromium from serpentinitic rocks/soils, and possible groundwater contamination by oxidative switch to its hexavalent form (Cr(VI)) is an environmental concern, due to poisoning effects on living organisms and human health.

Spring waters hosted in serpentinites may have high Cr(VI) contents, indicating a possible remobilization/ oxidation of Cr from the rocks into ground waters. However, the mechanisms of Cr(VI) release from serpentinites and serpentinitic soils are still debating and there is no clear relationship between its mobility and type of parental rock.

Here, we present our studies on spring waters hosted in Tuscan Serpentines belonging to the Ligurian ophiolitic Units (Northern Apennine). The concentrations of Cr (VI) in the sampled waters, range from 60  $\mu$ g/l in Querceto and Montecastelli sites to below the detection limit, in Santa Luce (Langone et al. 2013).

All the sampled springs are Mg-bicarbonate waters with alkaline pH values (6.5-8.5): the Cr(VI)-poor Santa Luce spring shows the highest values of Ca,  $SO_4$ ,  $SiO_2$  but the lowest Mg/Ca ratio compared to the other Cr(VI)-rich springs. Our petrological studies on selected rocks from the different areas aim to correlate the mineralogy of serpentinites with the geochemistry of the water. Spring waters with high Cr(VI) occur in areas of strongly carbonated serpentinites. At Montecastelli and Querceto, serpentinized dunites are intensely carbonated, with widespread formation of hydromagnesite, nesquonite and Mg-Fe layered double hydroxides (coalingite-pyroaurite; Boschi et al. 2017). The role of serpentinite carbonation on the mobilization/oxidation of chromium is investigated by on-going leaching experiments performed on crushed/milled aliquots of different serpentinites types.

# Serpentinites of the Sestri-Voltaggio, Palmaro-Caffarella and Voltri Units. Surface and drill core data from the "Gronda di Genova" highway by-pass

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*Keywords*: "Gronda di Genova" highway, petrography and micro-Raman spectroscopy of serpentine minerals, chrysotile-lizardite-antigorite veins.

The Genova highway by-pass will cross, for a length of about 15 km mainly in tunnel, meta-ophiolites located in the complex setting of the Sestri-Voltaggio Zone (Northern Italy, Alps-Apennines junction).

All along the planned by-pass, a number of rock samples have been collected from both outcrops and drill cores. From about two hundred representative rock samples, polished thin sections (about 30  $\mu$ m thick) have been studied by means of optical polarizing microscope and  $\mu$ -Raman spectroscopy for a reliable identification of serpentinite minerals.

Along the studied sections, two types of serpentinite have been recognized: antigorite (Atg) serpentinite in the western sector, and lizardite (Lz) serpentinite in the eastern sector respectively, separated by a sharp contact marked by slices of other lithologies.

In the less sheared Atg-serpentinites relics of the mantle peridotites are preserved, which indicate lherzolitic to harzburgitic protoliths. However, in both Atg- and Lz- serpentinites the original peridotitic microstructures are usually recognisable.

In the Atg-serpentinite, unusual cohesive heterometric tectonic breccias are exposed for a few km, consisting of serpentinite clasts cemented by a network of brownish chrysotile.

All serpentinites are cut by a complex network of veins, mainly consisting of either serpentine minerals or carbonates. The chrysotile and lizardite veins are ubiquitous all over the studied geologic sequence, whereas the antigorite veins are limited to the western sector. In particular, the antigorite veins are widespread as massive *en-echelon* lens-like domains, where antigorite exhibits a "fibrous" habit.

The petrographic study, supported by the  $\mu$ -Raman spectroscopy identification of serpentinite minerals, has given an important contribution to the field geology for defining the "asbestos-bearing petrofacies", rock groups distinguished on the base of their litho-structural features and characterized by different contents of fibrous minerals.

#### Multiple origins of methane in fluids circulating in the Othrys ophiolite, central Greece

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Keywords: continental serpentinization, hyperalkaline springs, bubbling and dissolved gases.

The complex geology of Greece includes two important parallel running ophiolitic belts. The Othrys Massif in central Greece belongs to westernmost of them. In and around this wide ophiolite outcrop, some cold hyperalkaline and some hypothermal (T < 40°C) alkaline springs are present. Thirty water samples were collected at 17 different sites and both bubbling and dissolved gases were analysed for their chemical (He, Ne, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub> and H<sub>2</sub>S) and isotope (He,  $\delta^{13}$ C-CO<sub>2</sub>,  $\delta^{13}$ C-CH<sub>4</sub>,  $\delta^{2}$ H-CH<sub>4</sub>) composition. All samples except one have H<sub>2</sub>S contents below detection limit (10 µmol/mol), whilst H<sub>2</sub> (from <2 to 2500 µmol/mol), CO<sub>2</sub> (up to 26,000 but generally below 1000 µmol/mol) and O<sub>2</sub> (up to 16,000 but generally below 3000 µmol/mol) present low concentrations. Gases in alkaline waters (pH <10) are generally dominated by CH<sub>4</sub> (from 128,000 to 915,000 µmol/mol), while hyperalkaline (pH > 11) waters are N<sub>2</sub> dominated (from 727,000 to 977,000 µmol/mol). Generally, He isotope composition excludes contributions from a mantle source, showing a mostly pure crustal contribution for the alkaline waters and a prevailing atmospheric contribution for the hyperalkaline ones.

Methane may have different origins, which can be subdivided in biogenic (either directly produced by microbial activity or deriving by decay of organic matter at T > 150°C) and abiogenic (from pure inorganic reactions). Among the latter, one of the most debated origins comes from serpentinization processes of ultramafic rocks in ophiolitic sequences at low temperatures (T < 80 °C). Furthermore, secondary processes (diffusion, inorganic or microbial oxidation, etc.) may mask the original chemical and/or isotope composition. Primary and secondary processes acting on CH<sub>4</sub> can be recognised mainly through its isotope ( $\delta^{13}$ C and  $\delta^{2}$ H) composition and the ratio between CH<sub>4</sub> and C<sub>2</sub>+C<sub>3</sub> hydrocarbons (Bernard ratio).

Samples collected in the Othrys Massif display a wide range of both isotope compositions of  $CH_4$  ( $\delta^{13}C-CH_4$  from -74.5 to -14.5 ‰ and  $\delta^2$ H-CH<sub>4</sub> from -343 to -62 ‰) and Bernard ratio (from 220 to 15,800). The relatively high values of the ratio seem to exclude great contributions from thermogenic  $CH_4$ . Alkaline waters present the most negative isotope values for  $CH_4$ , evidencing a biogenic (microbial) origin, whereas many of the hyperalkaline waters have  $CH_4$  isotope values are present, indicating sometimes a clear biogenic contribution. Finally, few samples both from alkaline and hyperalkaline waters show some evidence of secondary oxidation processes.

# Environmental problems related to serpentinites in the Pollino Geopark (Southern Appennine)

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Keywords: Asbestos-bearing serpentinites, amphiboles, inertization.

Recent publications have clearly showed the toxicity and carcinogenicity of asbestos-bearing serpentinites. Inhalation of asbestos-like minerals (chrysotile, crocidolite, cummingtonite-amosite, tremolite, anthophyllite) due to environmental exposure cause malignant mesothelioma and lung cancers. In particular, the serpentinites represent a serious environmental concern due to both the presence of asbestos-like minerals and the large Cr abundance that is prone to solubilisation as Cr(VI). At the Calabria-Lucania boundary (southern Apennines, Italy), ophiolitic rocks of the Frido Unit crop-out. In these rocks, the amphibole-like minerals (actinolite and tremolite) are typically intergrown with fibrous antigorite and chrysotile (serpentine mineral group). These minerals showing acicular, friable, fibrous, and elongated habitus can be easily released into the environment as a result of both natural processes and anthropogenic activities. In the analyzed rocks, the electron microprobe analysis (EMPA) revealed for the first time the presence of new amphiboles. Structural formula of amphiboles was recalculated on the basis of 23 oxygens and classified by using the amphiboles nomenclature suggested by Leake et al. (2004). The EMPA revealed that the average composition obtained on single crystals include Ca-amphiboles and Mg-Fe-Mn amphiboles. In particular, the calcic amphiboles include: edenite, magnesioferro-hornblende and canniloite while the magnesium-iron-manganese amphiboles is cummingtonite-grunerite (amosite). This cummingtonite-grunerite (amosite) in many cases is acicular to asbestiform in habit. Edenite is not considered as an asbestos-like mineral but a cluster of deaths from pleural mesothelioma was previously reported for Biancavilla, Italy, a city in eastern Sicily. A possible solution could be represented by mineral carbonation processes (Evans et al., 2013). Carbonation consists of an induced exothermic alteration of metalrich silicate minerals involving geologically and thermodynamically stable carbonate minerals. This process would lead to the inertization of asbestos-bearing serpentinites, CO, capture-storage and mitigate the risks of future climate change.

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# **Ophicarbonates from Mt. Pollino Massif (southern Apennines):** a possible use for geological sequestration of CO,

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Keywords: Ophicarbonates, serpentinites, stable isotope composition.

A comprehensive study of the ophicarbonate from northern sector of the Mt. Pollino Massif (southern Apennines, Italy) is here presented, in order to add constraints to the tectonic evolution of an important area of the southern Ligurian Tethys. Ophicarbonate formed by serpentinites-hosted carbonate-rich veins and by serpentinites-hosted talc-rich bodies associated with quartz and carbonate veins were collected at two different sites. Both ophicarbonate types derived from lherzolite protoliths and formed under blueschistfacies conditions to high pressure/low temperature (HP/LT) metamorphism but have different paragenesis. Ophicarbonate formed by serpentinites-hosted carbonate-rich veins (OFA) mainly consist of serpentine, amphibole minerals, hydrogarnet, titanite, diopside, clinochlore, magnetite and several carbonate phases (calcite, aragonite, rhodochrosite) whereas the ophicarbonate formed by serpentinites-hosted talc-rich bodies (OPp) are formed by serpentine, amphibole minerals, phyllosilicates, Cr-spinel, dolomite, Mg-calcite, and quartz. On the whole the ophicarbonate are characterized by  $\delta^{13}$ C fluctuations indicating a decarbonation trend which, in turn, means that carbonic fluids forming during prograde carbonate dissolution can flow along the slab interfaces promoting carbonate reprecipitation under favorable conditions. In detail, the OPps' samples are characterized by  $\delta^{13}$ C fluctuations coupled with a  $\delta^{18}$ O shift suggesting an open-system driven decarbonation trend at shallower crustal conditions during the exhumation. Fluid inclusions in the quartz show abundant aqueous and low salinity features (between 0.53 and 3.23 NaCl mass % equivalent) further supporting an open-system decarbonation. The OFAs' ophicarbonate, instead, developed in a closed-system between Upper Eocene and Lower Paleogene (50-53 Ma, <sup>87</sup>Sr/<sup>86</sup>Sr data) during the subduction of the slab. The OFA and OPp ophicarbonates thus formed at different times under similar environmental conditions from crustal-derived hydrothermal fluids at low-moderate temperatures having different chemical composition. The mineral assemblages represent evolving conditions of alteration, and an increase in variable activity of the carbonicrich fluids for OFA and of the carbonic-silica-rich fluids for OPp. Ophicarbonates from the Mt. Pollino Massif are the subject of a project devoted to their possible use for in situ geological sequestration of CO<sub>2</sub> starting from experiments in the laboratory (ex-situ sequestration).

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# Source and distribution of potentially toxic elements in serpentine soil profiles: a case study from the Voltri Massif (Liguria, Italy)

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Keywords: potentially toxic elements, serpentine soils, authigenic minerals.

Serpentine soils are important example of natural environmental issues due to their critical chemical and physical properties. In fact, they are generally characterized by deficiency of micronutrient (N, P, and K), low Ca/Mg ratio, and high contents of potentially ecotoxic elements (PTEs - e.g., Cr, Ni, and Co), commonly exceeding the concentration limits laid down by environmental agencies.

In this study we performed a complete mineralogical and crystallochemical characterization of soils and bedrocks from selected profiles, occurring in the metaophiolite of the Voltri Massif (Ligurian Alps), in order to: i) identify and quantify the PTEs-bearing minerals along soil profiles from different ultramafic bedrocks; ii) understand the fate of PTEs during the weathering process.

Soil samples were divided into three aliquots to separate the soil skeleton (2 mm-63  $\mu$ m) from the silt (63-2  $\mu$ m) and clay fraction (<2  $\mu$ m). Quantitative mineralogical analyses were performed by Rietveld refinement of XRPD patterns collected with synchrotron sources at the MCX beamline (Elettra Synchrotron). The chemical composition of the PTEs-bearing minerals was determined by means of EMPA-WDS and LA-ICP-MS. Major, minor, and trace element concentrations were analyzed via FP-XRF, ICP-EOS, and -MS.

The mineralogical variation from bedrock toward topsoil is mainly represented by the progressive decrease of serpentine minerals (from > 90 wt% to < 20 wt%) and spinels (from 1-5 wt% to < 1 wt%) with the concomitant increase of authigenic (mixed-layer chlorite-smectite and chlorite-vermiculite, goethite, amorphous Fe-oxyhydroxides) and allochthonous minerals (e.g. quartz and feldspars) which can represent over 50 wt% of the constituents within the topsoil.

PTEs are hosted mainly in the residual primary minerals deriving from the bedrock. Cr is mainly contained within spinels (magnetite, Cr-magnetite, ferrian chromite), chlorite and pyroxenes. Nevertheless, authigenic hematite and goethite can uptake non-negligible amount of Cr particularly in alteromorphs after spinels. The main Ni-bearing minerals are spinels and serpentine minerals. Significant Ni concentration was also observed in authigenic minerals, mainly represented by amorphous or low-crystalline Fe-oxyhydroxides and mixed-layer of clay minerals, which thus represent effective trap for Ni.

Chemically, the soil is generally depleted in Cr, Ni, and Co and enriched in Cu, Zn and V compared to the bedrock. Moreover, systematic decrease of Cr and Ni concentrations from subsoil to topsoil were observed in all the studied profiles, whereas Co and V tend to reach the highest concentrations within the topsoil.

Our study shows that the critical PTEs concentrations in the serpentine soil profiles are linked both to the residual bedrock-forming minerals and to their stable alteration products. These last, and in particular hematite, goethite and clay minerals, efficiently scavenge PTEs thus reducing their bioavailability.

# Concentrations and distribution of potentially toxic elements in ultramafic rocks from Ligurian ophiolites: influence of mineralogical, structural and textural features from different geological contexts

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Keywords: potentially toxic element, ultramafic rocks, ophiolite.

The knowledge on concentrations and behavior of trace metals in ultramafic rocks is of great interest for their petrological, geochemical and geodynamic significance. Nevertheless, they have also strong environmental implications since some of these metals are potential toxic elements (PTEs) which can be released to soil and circulating water during weathering and pedogenic processes.

The concentration and distribution of PTEs in ultramafic rocks is highly variable worldwide, since they can range up to two orders of magnitude mainly due to their geological setting and geodynamic evolution. In any case, these PTEs concentrations are commonly strongly higher than the limits of toxicity laid down by environmental agencies.

The aim of this study is to assess the role of local-scale lithological, textural and structural factors in the distribution of PTEs in different ultramafic rocks. For this purpose, we selected several ultramafic rock bodies with various degree of serpentinization and metamorphic overprint that crop out in the high-pressure metaophiolites of the Voltri Massif (VM) and in the low-grade ophiolites of the Val di Vara Supergroup (VVS). Mineralogy, microtextures and microstructures were investigated by optical microscopy, SEM-EDS, EMPA-WDS, and LA-ICP-MS. Bulk chemistry was carried out by means of FP-XRF, ICP-EOS, and ICP-MS.

Cr, Ni, and Co are invariably the PTEs with the highest concentrations throughout the studied sites although other metals (Mn, V, Ti, and Zn) are generally present in significant concentrations. Our results evidenced that VVS rocks are systematically enriched in PTEs compared to VM rocks. Nevertheless, substantial differences in PTEs distribution were observed within the same ophiolite complex and even at the scale of the single outcrop. Ni tends to decrease according to degree of serpentinization and deformation, showing the highest values in partially serpentinized peridotites and the lowest in foliated serpentinites. Conversely Cr and, subordinately, Co are mainly influenced by the deformation degree with massive serpentinites showing the highest contents. Ti and V, being hosted mainly in magnetite and ilmenite, increase significantly in serpentinites occurring close to tectonic contacts with other lithotypes (eclogites, gabbros and metasediments).

In conclusion, our study shows that at a general scale the PTEs variability is primarily related to the petrologic and tectonic evolution but, at a local scale, also the mineralogical, lithological, structural, and textural features correlated to the degree of serpentinization and/or deformation significantly influence their distribution and concentration. These evidences have important environmental repercussions since the substantial differences can directly affect soil chemistry as well as PTEs mobility and bioavailability. Furthermore, this study should be the preliminary step for the evaluation of background concentrations for naturally occurring contaminants.

### Geogenic chromium in natural waters interacting with serpentinite rocks: preliminary study on treating by nanofiltration membranes

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Keywords: Chromium, natural waters, serpentinite rocks.

Chromium (Cr) is a dangerous element which occurs into rocks, soils and groundwaters. The abundance in the natural system mainly depending on availability into bedrock. In details, the highest concentrations of total Cr were detected in ultramafic, serpentinite rocks and their derived soils made up of Cr-minerals such as minerals of spinel group, olivines, pyroxsenes and serpentine where Cr is present in variable amount; Cr-rich groundwaters are the results of weathering processes of this minerals (Fantoni, 2002; Kazakis, 2015). The WHO drinking water guideline for total Cr has been set to 50 µg/L and it has been adopted by many countries but starting from 1 January 2019 the potability threshold value for Cr (VI) will be lowered to  $10 \,\mu g / 1$ (D.M. 06/07/2017) by Italian government. The aim of this work was treat Cr- rich groundwaters through nanofiltration membranes as alternative to conventional methods (Frank, 1996). In this regards nanofiltration (NF) laboratory-scale system with membrane modules named DK (proprietary thin-film) were used to treating polluted groundwater. The sample water comes from Bonassola serpentinitic aquifer (La Spezia, Liguria, Italy) and the Cr concentration detected was 84 µg/l, present as Cr (VI). Experiments were conducted at different operating pressure (5 bar, 10 bar, 15 bar), evaluating the permeate flux. Permeate sample, for each experiment, was collected to evaluate Cr-rejection. The analyses have shown high rejection (above 95%) for each operating pressure investigate, lowering Cr (VI) concentration within the limits established by law. NF treatment was already tested in synthetic solutions of Cr and the results obtained in this work are much promising for future developments on treating of polluted natural water, premising drinking use in the contaminated areas.

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# An atypical occurrence of asbestiform sepiolite associated to aliphatic hydrocarbons from Sassello (Ligurian Apennines, Italy): mineral-petrographic characterization and possible hazards

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Keywords: sepiolite, aliphatic hydrocarbons, Fischer-Tropsch-type reaction.

An unusual occurrence of asbestiform sepiolite, filling veins in the antigorite serpentinities of the Voltri Unit, exposed in a borrow pit (nowadays reclaimed) in the Deiva forest, near Sassello (NW Italy), was characterized with an in-depth analytical approach, aimed at studying its crystal-chemistry and structure and evaluating its possible hazards for human health. To the naked eye, this sepiolite has an evident fibrous habit, with fibres apparently up to several cm long. When observed with optical microscopy and SEM-EDS, however, these macroscopic fibres proved to be made by bundles of thinner fibrils (average length > 100  $\mu$ m; thickness  $\approx$  80 nm), with a crystal-chemistry consistent to that reported in literature. Dehydration of this sepiolite sample was monitored through TGA and FT-IR, performed at increasing temperatures. The latter approach, in particular, evidenced presence of moderate amounts of aliphatic hydrocarbons - not yet thoroughly identified - somehow associated to the fibres. The refinement of the crystal structure, performed with the Rietveld method, showed no significant difference from the literature models, but a peculiar distribution of zeolitic H<sub>2</sub>O inside the framework nano-tunnels was observed. The geological context suggests that the Sassello sepiolite precipitated from low-temperature hydrothermal fluids, which were saturated in Mg and silica by a prolonged interaction with the host rocks (serpentinities and partly serpentinized lherzolites). The same setting favoured formation of the associated abiotic hydrocarbons, by means of the Fischer-Tropsch reaction. The extremely long and flexible fibrils of this sepiolite specimen (length/width aspect ratio >> 3, as inspected by SEM) could represent a serious hazard for human health if air dispersed and breathed. In addition, its atypical association with hydrocarbons (only once reported in the literature: Giustetto et al., 2014) might even favour further fragmentation in thinner units, thus increasing its potential noxiousness.

Giustetto, R., Seenivasan, K. & Belluso, E. (2014): Asbestiform sepiolite coated by aliphatic hydrocarbons from Perletoa, Aosta Valley Region (Western Alps, Italy): characterization, genesis and possible hazards. Mineralogical Magazine, 78(4), 919-940.

CONGRESSO SGI-SIMP 2018

# Multi-instrumental investigations on asbestos minerals and their non-asbestiform analogues: inferences from host rock textural constraints

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Keywords: asbestos and asbestiform minerals, multi-instrumental approach, environmental monitoring.

Asbestos as hazardous minerals is a well-known and common issue worldwide. Amphiboles and other Elongated Mineral Particles (EMP) not classified as asbestos are even more common but their potential hazard is not fully understood. A debate about including or excluding in counts the minerals chemically and geometrically (length  $>5\mu$ , length: diameter >3:1) but not morphologically analogous to normed asbestos is still open and current. This is a delicate topic and the choice of a counting method remains a technician concern in quantitative assessment, in order to define whether the Asbestos Containing Materials (ACM) can be reused as a by-product (concentration <1000 mg/kg) or must be managed as special waste (concentration >1000 mg/kg). The aim of this work is to investigate by a multi-instrumental approach, at different observation scales, the influence of textural constraints in massive samples in determining the subsequent origin of asbestiform or not asbestiform products. This aspect has an obvious fallout on diagnostic strategies addressed to environmental monitoring. The samples, strategic to this question are: a serpentinized peridotite (S1; Piedmont, Italy), a tremolite and calcite vein associated with a serpentinite (S2; Aosta Valley, Italy), a metabasalt (S3; Piedmont, Italy) and a pyroxenite (S4; Gauteng, South Africa). These samples were selected being lithotypes with different petrological evolution and because the identification and characterisation of the fibrous phases is challenging. Samples were analysed by Optical Microscopy (OM); Scanning and Transmission Electron Microscopy (SEM and TEM) and Synchrotron Radiation X-ray microtomography (SR X-ray µCT). Paradoxically, the identification of the asbestos phases is easy by OM but even at higher magnifications a fibrous habitus has the same geometric parameters of prismatic/acicular crystals. Under SEM it is possible to better characterise the geometric ratios and the textural relations between the various phases: sometime is possible appreciate the habitus, but it is often difficult to discriminate serpentine polymorphs. TEM investigation allowed the highresolution discrimination for EMP and a better discrimination between regulated and non-regulated asbestos. Therefore, integrating all the techniques, analysed samples result mainly composed by chrysotile and fibrous antigorite (S1); acicular associated to less fibrous tremolite and rare chrysotile (S2); acicular to prismatic actinolite (S3); prismatic and acicular amphibole of the actinolite-tremolite series (S4). In addition, SR X-ray µCT permit a better rock textural discrimination towards a classification improvement for regulated and nonregulated asbestos. However, individually, none of the techniques is adequate to unique and time-efficient identification of the fibrous and asbestiform phases, especially if they occur in massive rocks and therefore not isolated.

### Preparation of tremolite samples for in vitro studies

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Keywords: tremolite, stationary test in vitro, SEM analysis.

The ophiolites, commonly known as greenstones due to their typical colouring, may contain asbestos; they represent a grouping of rocks of magmatic origin which characterize, in the form of outcrops, numerous areas in almost all continents. In Calabria, in the south of Italy, the ophiolitic sequences are located in Mount Reventino area. The most common type of asbestos detected in these rocks was tremolite. The aim of our study was to prepare and characterize samples of tremolite coming from these rocks for in vitro studies. The samples chosen were those collected in Platania, Mount Reventino area. The samples had two distinct phases: the first one was talcose (white) and the second one green with compact nature. The analytical techniques used, showed that the white powdered phase similar to talc was tremolite. To isolate the white phase of the mineral, a careful examination under stereomicroscope was necessary and with the help a spatula the white phase was collected on a porcelain crucible. The collected powder was heat-treated in a muffle furnace at 450°C for 12 hours (Campopiano et al., 2015). The sample was analyzed by dispersion stain and phase contrast optical microscope (PCOM), infrared Fourier transform spectroscopy (FTIR), and scanning electron microscopy (SEM). The analysis confirmed that the powder was tremolite and could be used for in vitro experiments. A stationary test in vitro under simulated physiological conditions was carried out. To simulate extracellular environment and macrophage environment we used a Gamble's solution to two different pH, respectively 7.4 and 4.5 (Campopiano et al., 2014). A small amount of fibers were subjected a treatment in saline solution at 37°C from 1 to 4 weeks. SEM analysis of samples not showed morphological and size changes. The mean diameter, the mean length of tremolite fibers, and the percentage of respirable fibers after 28 days of treatment did not show changes compared to untreated sample. These first results showed an insolubility of tremolite fibers. The study will continue for measuring the dissolution constant.

Campopiano, A., Cannizzaro, A., Angelosanto, F., Astolfi, M.L., Ramires, D., Olori, A., Canepari, S. & Iavicoli, S. (2014): Dissolution of glass wool, rock wool and alkaline earth silicate wool: Morphological and chemical changes in fibers. Reg Tox Pharm, 70(1), 393-406.

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# Occurrence of hexavalent chromium in groundwater in the northern sector of the Pollino massif, southern Italy

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Keywords: hexavalent chromium, groundwater, Pollino massif.

Chromium (Cr) is a heavy metal that naturally occurs in the Earth's crust but is also produced by manufacturing processes for stainless steel, chrome plating, dyes, pigments and wood preservation. Regarding its natural origin, mineral leaching of ultramafic/ophiolitic rocks can be considered the main cause of chromium occurrence in groundwater. Ultramafic/ophiolitic complexes host Cr mainly in chromite and silicates (olivine, pyroxenes or serpentine) and are widespread in the Mediterranean area (i.e. Italy, Greece, Cyprus, Turkey). The behavior of the chromium depends on the valance or oxidation state. Cr(III) is the predominant form in most minerals and is favored by reducing and strongly acidic conditions, while Cr(VI) occurs under oxidizing and alkaline conditions. The Cr form in the environment is of ecological and public health significance, since Cr(III) is insoluble at pH> 5, immobile and with relatively low toxicity, while Cr(VI) is very soluble, mobile and a human carcinogen. In this work total dissolved Cr, Cr (VI), some trace elements and isotopic data  $(\delta^{18}\text{O and }\delta\text{D})$  were determined in groundwater of northern sector of the Pollino massif (southern Italy) in order to verify occurrence and distribution of the Cr. These results are part of a larger project (entitled CrITERIA-T3ERA-00004) funded by ERANETMED Joint Call on the Cr geogenic and anthropogenic origin in groundwater from Mediterranean area. The Pollino Massif is included in the area of the Pollino National Park, where the effect of anthropogenic pollution is negligible. The investigated area is characterized by terrains of the Ligurian Complex tectono-stratigraphic unit composed of two ophiolite bearing units (the Calabro-Lucanian Flysch Unit and the Frido Unit). Ophiolitic rocks consist of lenticular metabasites interbedded with cataclastic and highly fractured serpentinites. Pyroxenes in metabasites are replaced by chlorite, actinolite, epidotes, titanite, and Fe-oxides. In the investigated area two different hydro-facies are observed, reflecting low-temperature water-rock interactions. The first water type has Mg-HCO, composition, resulting from the interaction between meteoric waters and serpentinites, whereas the second one has Ca-HCO<sub>2</sub> composition due to the interaction with Ca-rich rocks (i.e., carbonate rocks, and metabasites). Trace elements are below maximum admissible concentrations by Italian legislation (D-Lgs 31/2001 for drinking use) but for Cr and Cr (VI) in ten springs and for Ni in only one water sample. The measured values are higher than those previously reported from Margiotta et al. (2012; 2014) in the same area, suggesting that the increase of Cr(VI) pollution is probably due to natural factors (e.g. longer and/or slower hydrogeological circuits) rather than to a seasonal variability. The isotopic data seems to confirm their meteoric origin of water, although, at the present stage, they do not allow us to check variations linked to the seasonal component.

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# Geochemical and mineralogical features of serpentinite-derived soils in southern Italy: prospect for hazardous exposure

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Keywords: Natural Asbestos Occurrences, serpentinite soil, heavy metals.

A suite of serpentinite rocks and related soil samples developed have been investigated in order to understand their possible contribution to health problems caused by asbestos exposure. In particular, attention focused on the village of San Severino Lucano (Basilicata region, southern Italy), because of its geographic insulation from large urban centres as well as industrial and/or commercial plants, that likely exclude sources of asbestos and asbestiform minerals other than those ones related to the local geological features. This permitted to pay attention to NOA (Naturally Occurring Asbestos) and to better understand the consequences on population.

Agricultural soil samples as well as serpentinite mother-rocks have been collected at the village centre and characterized by using different analytical techniques such as Optical microscopy, XRF, XRPD and SEM/EDS. Results highlighted that all of the collected soil samples contain asbestos minerals (*e.g.*, chrysotile asbestos, tremolite-actinolite) clay minerals, plagioclase and oxides in various amounts. Moreover, preliminary geochemical investigation aimed to quantify the heavy metals content in rocks and soils, pointed out that four toxic elements (Cr, Co, Ni, V) in almost all the specimens exceeds the regulatory thresholds for public, private and residential green use.

In conclusion, since the dispersion of fibres could be associated with carcinogenic lung cancer, in our opinion in those areas where NOA can be found, the institutions should publish local maps indicating areas with mineralogical concern and take precaution.

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# Degradation of mortars containing aggregate rich in serpentinites: the case of industrial brick masonry

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Keywords: asbestos, light-weight masonry mortars, decay of mortars

The risk of asbestos exposure (European Directive 1999/3/CE) is generally assessed for the C&D waste (Construction and Demolition), for the asbestos cement (eternit) used as building materials (plates, pipes, floor) and for the asbestos textile used for thermal insulation in the industrial sectors and in fire protection barriers. The evaluation of risk for dispersion of asbestos fibres in the atmosphere due to degradation of lime mortar containing aggregate rich in serpentinite is rarely analysed.

The aggregate containing fibrous minerals in light-weight masonry mortars was used in the industrial building of '900 to reduce the average density and thermal conductivity and to increase the physico-mechanical. The big development of constructions in the 20th century promoted the experimentation of innovative solutions to improve the performance of industrial buildings and in particular the industrial brick masonry chimneys and furnaces.

The use of sand rich in fibrous minerals is one of these innovative technological solutions. It was adopted in the beginning of the 20th century to realize the sugar factory that it was in use until 1968 and that is now the Technological Scientific Pole of University of Ferrara. That sugar factory is a symbol of the industrial history of the Po River Plain, so it is protected by the Italian Ministry of Cultural Heritage (Minghini et al., 2016).

As a result of the petrographic study of the mortars, they were classified as a mixture of lime and cement and an aggregate consisting of silicate sandstones, carbonate and fragments of ophiolite rocks (tholeiitic basalts and serpentinites). Considering the composition of the rocks and the geographic location of the sugar factory, it is possible that the sand was extracted in the Sillaro River area (Benini & Guasti, 1992).

The use of sand rich in fibrous minerals precedes the introduction of the filler and of the asbestos textile in the cements and mortars to improve their technological performance. The study of mortars has shown their high propensity to crack due to salt crystallization, frost stress and biological degradation, so the mortar durability is lower when they are deprived of the protective layer of the plaster.

Minghini, F., Bertolesi, E., Del Grosso, A., Milani, G. & Tralli, A. (2016): Modal pushover and response history analyses of a masonry chimney before and after shortening Engineering Structures, 110, 307-324.

Benini, A. & Guasti, M. (1992): Carta geologica dell'Appennino emiliano-romagnolo. Sezioni n. 238060 "S. Clemente", 238090 "Bisano", 238130 "Frassineto". Regione Emilia- Romagna, ufficio Cartografico. S.EL.CA., Firenze.

# Tremolite-bearing marbles from Namibia exploited as dimension stone: preliminary mineralogical and petrographic characterization

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Keywords: Marbles, tremolite, dimension stone, quarries.

Many varieties of marbles rich in magnesium are exploited and marketed as dimension stones all over the world.

In the present paper, we deal with marbles cropping out in Namibia, which are quarried and marketed as "White Namibia". A comprehensive investigation was carried out on marble specimens coming from various quarries.

In particular, we carried out petrographic investigation with optical microscope together with XRD characterization, microRaman and Scanning electron microscopy (SEM) analyses.

These marbles are ascribed to the Karibib formation, that includes medium to high-grade metamorphic rocks. At the hand specimen scale, marbles are white, with "saccaroid"-like features and in some cases cut by yellowish veins.

At the microscale. white marbles are rich in lepidoblastic felts made up of calcite+ whitish tremolite+dolomite+talc assemblage. Calcite and dolomite constitute the granoblastic portion. Moreover, SEM analysis revealed that tremolite within veins may be characterised by fibrous habitus, since tremolite crystals are prone to crumble and split into thinner individuals.

Tremolite is included within the asbestos minerals by WHO (i.e. World Health Organization WHO 1986); indeed, fibrous tremolite is a potential pollutant material since its inhalation due to environmental exposure could cause malignant mesothelioma and lung cancers. Fortunately, only some mining areas have levels rich in tremolite and the census of these levels can avoid the opening of quarries in places unsuitable for the marketing of marble. The petrographic surveys returned in thematic geopetrographic maps will allow to locate the areas suitable for extraction and to place extraction bans in the areas rich in asbestos tremolite. The certification of petrographic and geochemical characteristics of the tremolite-free lithotypes can protect this emerging sector of the economy of Namibia, the health of quarrymen and certify the suitability of use of the marbles.

For the above reasons, the present work aims to characterise the uncommon level of White Namibia marble, in order to prevent negative health effects related to eventual hazardous exposure to asbestos tremolite.

Bloise, A., Punturo, R., Catalano, M., Miriello, D. & Cirrincione, R. (2016): Naturally occurring asbestos (NOA) in rock and soil and relation with human activities: The monitoring example of selected sites in Calabria (southern Italy). Italian Journal of Geosciences,135(2), 268-279. doi:10.3301/IJG.2015.24.

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World Health Organization, (1986): Asbestos and other natural mineral fibres. Environmental Health Criteria, 53. Geneve.

# Geochemical and hydrogeological characterization of the metamorphic-serpentinitic aquifer of the Coreca area (Calabria, South Italy)

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Keywords: metamorphic-serpentinitic aquifer, Mg-HCO3 groundwaters, Ca-HCO3 groundwaters.

Calabria Region is characterized by a wide compositional variability of water resources due to its complex geological, hydrogeological and climatic context. Because of lithological arrangement and/or anthropogenic contaminations, the Calabrian resource is sometimes affected by quality degradation. An example is the area of the Oliva catchment, which includes Coreca (the site object of this work), seaside tourist resort where, in the last few years, were carried out several surveys due anomalous values detected in the environmental matrices.

As reported by Italian newspapers, along the area, geochemical surveys highlight anomalies in cesium, beryllium, cobalt, copper, mercury, zinc, antimony, manganese, cadmium, vanadium higher than those imposed by both Italian law (D.lgs. 152/2006) and World Health Organization (WHO, 2004).

To improve the knowledge of the metamorphic-serpentinitic aquifer of the Coreca area (Calabria, south Italy), 23 groundwater samples were collected and a hydro-geochemical study was carried out. Geological and structural characteristics suggest the presence of three main aquifers: i) a first metamorphic ophiolitic aquifer located above slates belonging to the Frido Unit (Critelli et al., 2015), ii) a second metabasitic aquifer and iii) a third aquifer hosted in the Miocene Carbonate deposits (Muto & Perri, 2002).

Geochemical results allowed to identify groundwater characteristics and reconstruct the hydro-geochemical model. Two groups of waters were identified. The first Ca-HCO<sub>3</sub> group suggesting a strongly control of Ca-rich minerals dissolution, which characterize either metabasalts and Miocene rocks. The second Mg-HCO<sub>3</sub> group related to an interaction of meteoric water with the serpentinite rocks of the Frido Unit.

Finally, values of major and trace elements have been compared with the Italian law limit values and the drinking water guidelines provided by World Health Organization (WHO). Only samples S20, S25 and S29 have shown a Mn and Ni contents higher than the Italian law threshold. Overall, the obtained data indicate a good quality of aquifers in the studied area.

Critelli, T., Vespasiano, G., Apollaro, C., Muto, F., Marini, L. & De Rosa, R. (2015): Hydrogeochemical study of an ophiolitic aquifer: a case study of Lago (Southern Italy, Calabria). Environmental Earth Science, 74, 533-543.

Muto, F. & Perri, E. (2002): Evoluzione tettono-sedimentaria del bacino di Amantea, Calabria occidentale. Bollettino Società Geologica Italiana, 121, 391-409.

# Session S30 Geosciences for Cultural Heritage

Conveners AND CHAIRPERSONS Fabrizio Antonelli (Università IUAV, Venezia) Alberto De Bonis (University of Wien, Austria) Domenico Miriello (Università della Calabria) Simona Raneri (Università di Pisa)

# The provenance of the obsidian artefacts from the Middle Kingdom harbour of Mersa Gawasis, Red Sea, Egypt

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Keywords: Obsidian, Egypt, Mersa Gawasis.

This paper explores ancient trade routes between Egypt and the Horn of Africa and the network distribution and procurement areas of obsidian, through the geochemical analysis of obsidian artefacts found in the archaeological site of Mersa Gawasis, a Middle Kingdom harbour located along the Egyptian Red Sea coast. Six artefacts were geochemically characterized and compared with the obsidian geologic sources of the Horn of Africa and the Arabian peninsula. The major element concentrations were determined by SEM-EDS analysis and the trace element concentrations were obtained by the LA-ICP-MS method, an almost non-destructive technique, capable of chemically characterizing the volcanic glass. A comparison of geochemical results obtained on the archaeological artefacts and bibliographic data of geological sources allows us to determine the provenance of all obsidian finds. At first, all archaeological finds show Th/Ta ratios lesser than 5 suggesting a possible provenance from the Ethiopian, Eritrean, Yemenite or South-Western Saudi Arabia obsidian sources. Then, the new geochemical data, compared with the existing bibliography, highlight that two archaeological samples come from the Yemenite volcanic area of Dhamar Reda. The other four samples show a geochemical similarity with Eritrean geological obsidian.

If at the moment there is no reliable information on the presence of maritime traffic over long distances during the Egyptian late prehistory, the data coming from Mersa Gawasis strongly reiterates the role of the Red Sea, as a preferential way of traffic between Egypt and the Horn of Africa, at least starting from the Old Kingdom.

### Non-destructive chemical and mineralogical analysis of Etruscan Painted Architectural Slabs

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Keywords: XRD spectroscopy, micro-Raman spectroscopy, Cerveteri archeological site.

In 2016 a huge amount of archeological materials, mainly painted architectural slabs, were retrieved from the Glyptotek of Copenhagen and the private collection of R. Syme thanks to an action of the Comando dei Carabinieri della Tutela Patrimonio Culturale. According to the analogies in style and the typology part of these materials are supposed to come from the UNESCO archeological site of Cerveteri, important Etruscan center to which belong a large amount of materials dated back to the second half of the VI century B.C. Due to the importance of these precious terracotta, all the specimens were investigated by means of non-destructive portable XRF and Raman instrumentations. Furthermore, XRD and micro-Raman spectroscopy were carried out on micro-samples picked up by the restorers of Superintendence. The research aims are: i) the individuation of the main chemical and mineralogical composition of the pottery bulk; 2) the characterization of the painted layers. The data obtained were compared with those carried out on similar fragments certainly attributed to Cerveteri and Veio. Furthermore, the use of pigments was related to the colors used in the archaic period for the Tarquinia (Barone et al., 2018) wall painted tombs.

The slabs, all with a creamy engobe, show human and animal figures in geometrical frameworks. Combined Raman and XRF analysis allowed us to distinguish different pigments and to suggest some considerations about their authentication.

Barone, G., Mazzoleni, P., Cecchini, A. & Russo, A. (2018): In situ Raman and pXRF spectroscopic study on the wall paintings of Etruscan Tarquinia tombs, Dyes and Pigments, 150, 390-403.

#### Potentiality of ghiara as geopolymer raw material and its application in Cultural Heritage

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Keywords: Geopolymers, local building material, thermal analyses.

The object of our studies is the use of a particular paleo-soil present in below the lava flow in the Mt. Etna region, locally named "ghiara", in the production of geopolymers. Indeed, in XVIII-XIX centuries, this material was appreciated for its reddish colour and pozzolanic behaviour (Belfiore et al., 2010) so to be widely used as aggregate in mortars in Catania architecture (Sicily). However, ghiara has negative performances if not well mixed with lime, causing decay forms, such as detachment and crumbling due to cohesion problems observed in old buildings of historical interest. In last decades, the restorations of historical constructions with this material are largely required to revamp Catania historical centre. However, in the last decades, restoration works of old city were carried out with use of improper and not eco-friendly materials. This last is an important feature required also in restoration works. For this purpose, we investigated the potentiality of ghiara material for geopolymeric formulations by alkali activation in Cultural Heritage field.

In detail, after the wide mineralogical and chemical characterization of the raw materials performed by XRD and XRF (with portable equipment) analyses, we used ghiara powder as aluminosilicate source in the formulation of geopolymeric pastes. Due to the ghiara low reactivity, we carried out thermal treatments on geopolymers cured at ambient temperature  $(22 \pm 3^{\circ}C)$  up to temperatures of 400°C (Kamseu et al., 2009). With the aim to better understand the thermal behaviour, we performed thermal analyses (DTA/TGA and optical microscope) of both geopolymer and ghiara raw material. The results of this latter showed a shrinkage occurring during the sintering process in the range from 900°C to 1400°C, whereas the densification from 1100 to 1200°C. In the other hand, the geopolymer results pointed out densification process started before in the range from 900°C to 1100°C, so it resulted more fusible than the raw material due to the presence of alkaline ions.

On the whole, the results confirmed the importance of thermal treatments on raw material to make it active to geopolymerization, although we hope to find a different way to reduce treatment temperatures for a low environmental impact. According to our results, this material has a good chance to be used in alkali activation process for Cultural Heritage field. However, further analysis and tests had to carry out to complete the study of this material.

Belfiore, M. C., La Russa, F. M., Mazzoleni, P., Pezzino, A. & Viccaro, M. (2010): Technological study of "ghiara" mortars from the historical city centre of Catania (Eastern Sicily, Italy) and petro-chemical characterisation of raw materials. Eviron Earth Sci, 61, 995-1003.

Kamseu, E., Leonelli, C., Perera, D.S., Melo, U.C., & Lemougna, P.N. (2009): Investigation of Volcanic ash based geopolymers as Potential Building Materials. InterCeram:Internation Ceramic Review, 58(2-3.), 136-140.

# Artificial Neural Network for the provenance study of archaeological potteries using clay sediment database

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Keywords: archaeometry, pottery, clayey sediments.

A feedforward neural network (NN) for archaeometric studies has been created to facilitate provenance attribution of archaeological ceramics. A multilayer perceptron model (MLP) has been applied to construct the network, including only one hidden layer. Moreover, correction parameters based on historical information has been applied to Bayesian probability factor.

The NN has been trained by using clays mixings mathematically constructed using a reference chemical database of Sicilian sediments. The clay mixing take in consideration compositional variability within the same geological site and ceramic production processes. Test has been performed by querying the NN with compositional data of pottery assemblages found in the archaeological sites of Agrigento, Gela, Siracusa, Lentini, Catania and Milazzo coherently with clays sampling areas. Up to 88% correct attribution has been verified, with flawless correspondence between geological and archaeological contexts.

Merits of NN have been finally highlighted, comparing the extent of successfully provisional attribution with results achievable by using classical multivariate statistical method (PCA and LDA).

# Non destructive XRF analysis of Egyptian and Egyptian style amulets coming from Sicilian archaeological sites

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Keywords: portable XRF instrumentation, provenance studies, soapstone and faience.

The purpose of this research is to examine the Egyptian and Egyptian style amulets which since the Archaic period (8th century b.C. until the first half of the 6th century b.C) have influenced ancient Sicilian cultures.

The presence of Egyptian or Egyptian like amulets can be attributed to the intense trade exchanges in the Mediterranean Sea in the Archaic period including the Aegean area, Southern Italy and Pithekoussa.

Aegyptiaca are composed of scarabs in stone or faience, statuettes of deities and faience unguentaria. They help us to understand the connection between Egypt and other Mediterranean cultures.

The Aegyptiaca, which this project deals with, were found in the archaeological site of the Syracuse area, Central Sicily (Monte San Mauro and Aidone) and Lipari island. All the specimens are currently preserved in the regional archeology museum Paolo Orsi in Syracuse and in the regional Aeolian museum Bernabò Brea of Lipari.

The production of scarabs of the 7th century b.C., Orientalizing Period, can be divided into two groups: authentic Egyptian objects produced in Egypt and Egyptian-style objects produced in the Greek area by artisans from Rhodes, mainland Greece and the Middle East area.

This study applied non-destructive analysis (XRF) to artifacts of presumed Egyptian or Egyptianizing origin with the aim to identify production sites and therefore indicate probable trading routes.

#### **Portable XRF analysis for the study of Sicilian flint archaeological tools**

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#### Keywords: pXRF, Flint, Sicilian Prehistory.

The use of non-destructive techniques has exponentially increased the requests of quantitative analysis by the archaeologists and it has expanded the impact of provenance studies in archaeology. The portable XRF technology has proven useful for the study of many materials (metals, ceramics, precious stones) (Liritzis & Zacharias, 2011; Barone et al., 2017), and its popularity amongst the researchers is due to some characteristics of the analysis protocol: it is fast, portable and non-destructive.

In the last decade, different papers have explored and debated about the reliability of pXRF for the characterization of flint and obsidian (Olausson et al., 2017; Tykot, 2017a), the three main raw materials in use during the prehistory for the creation of instruments.

A study of provenance rises many questions that go over the simplistic answers about the localization of a quarry or the area of procurement: is there a territorial control? is the access to the resources restricted? What are the direction and the frequency of movements? And so on.

From the Mesolithic onward, raw material procurement strategies became more complex, and flint and obsidian were exploited and exchanged both locally and in distant localities.

The pXRF in Sicily was used to understand the role of the obsidian in Prehistory (Tykot, 2017b) but it had never been employed to analyze flint. In this preliminary study, we tried to differentiate flint collected in the Hyblaean Plateau, with the aim to find which are the best element to discriminate different sources of procurement, and to see if there is a link between visual and chemical characterization. In a near future, using these first results, we will analyze different archaeological instruments coming from different context of South-Eastern Sicily.

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Olausson, D., Hogberg, A. & Hughes, R. E. (2017): The use of non-destructive energy dispersive x-ray fluorescence (EDXRF) analysis for sourcing flint in Northern Europe: progress to date and prospects for the future. In: Pereira, T., Terradas, X. & Bicho, N. Eds., The exploitation of raw material in Prehistory: sourcing, processing and distribution, 98-112, Cambridge.

Tykot, R. (2017a): A Decade of Portable (Hand-Held) X-Ray Fluorescence Spectrometer Analysis of Obsidian in the Mediterranean: Many Advantages and Few Limitations. MRS Advances, 2(33-34), 1769-1784.

Tykot, R. (2017b): Obsidian studies in the prehistoric central Mediterranean: After 50 years what have we learned and what still needed to be done? Open Archaeology, 3, 264-278.

# Sicilian and Southern-Italian red-figure potteries: a provenance study on findings from Gela by portable X-ray fluorescence

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Keywords: Sicilian and Southern-Italian red-figure vases, Gela, portable X-ray fluorescence.

In this contribute we present an archaeometric study carried out by non-destructive method on a selection of red-figure vases datable between the second half of the fifth century B.C. and the beginning of the third century B.C., and found at Gela, an important Greek colony on the southern coast of Sicily.

This class of vessels includes valuable artifacts, found in different archeological contexts through Sicily and Southern Italy and preserved in several Museums. So far, scholars have attributed hypothetically these vases to single painters only on the basis of the drawing style and the iconography of the depicted scenes (Trendall, 1989) and they have made assumptions about the location of the different workshops merely according to the distribution of findings (Barresi, 2014; Denoyelle & Iozzo, 2009; Spigo, 1987). The only archaeometric study on the provenance of these ceramics is a recent research on vases from the archaeological site of Locri Epizephiri (Mirti et al., 2004). However, the possibility to address a more comprehensive investigation about location of production centers and to reconstruct the production system and the circulation of the fine vessels would require the collection of several archaeometric data on red-figure vessels variously founded in different archeological contexts and attributed to as many as painters.

The occurrence of both figured vases in excellent conditionand small fragments attributed to famous painters often does not allow the sampling. In the matter in question, the application of non-destructive approach is advisable. For the aforementioned, a selection of red-figure vases preserved at the Archaeological Museum of Gela (Sicily) and stylistically attributed to several painters whose activity has been localized both in Sicily and in South-Italy, have been analyzed by portable X-ray fluorescence method. In detail, measurements have been carried out on both bulk and red surface though a Brucker portable XRF spectrometer (Tracer IV-SD). The obtained results have been processed by statistical methods with the aim to differentiate the provenance of the studied artifacts on chemical bases.

Barresi, S. (2014): Sicilian Red-figure Vase-painting: The Beginning, the End, in Sabetai V. & Schierup S. (Eds.), The Regional Production of Red-figure Pottery: Greece, Magna Graecia and Etruria, Aarhu, 235-354.

Denoyelle, M. & Iozzo, M. (2009): La céramique grecque d'Italie mériodionale et de Sicile. Productions coloniales et apparentées du VIIIe au IIIe siècle av. J.-C.-, Paris.

Mirti, P., Gulmini, M., Pace, M. & Elia, D. (2004): The provenience of red figure vases from Locri Epizefiri (Southern Italy): new evidence by chemical analysis. Archaeometry 46(2), 183-200.

Spigo, U., (1987): La ceramica siceliota a figure rosse: variazioni sul tema. Bollettino d'Arte LXXII, 44-45, 1-24. Trendall, A.D., (1989): Red Figure Vases of South Italy and Sicily a handbook, London.

# Microfacies analyses applied to building stones: the Pleistocene Gravina Calcarenite (Matera, southern Italy)

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Keywords: diagenesis, soft limestone, degradation behaviour.

Limestones of the Pleistocene Gravina Calcarenite Formation have been excavated and used to build the Matera old town, Sassi. It is one of the oldest rupestrian settlements recognized as a Unesco site in 1992. Actual degradation of the building stones represent a serious problem for the safeguard and protection of the site. For this reason, a precise characterization of the calcarenite and the knowledge of its diagenetic alteration is necessary for a suitable preservation. The Gravina Calcarenite Formation consists of a carbonate succession made up of predominantly lithoclastic or bioclastic calcarenites, intrabasinal biocalcarenites and biocalcirudites. The aim of this work is to provide microfacies data of the Gravina Calcarenite, through analysis with optical microscope, SEM and CL, for understanding its microtextural features, especially those which are important parameters for the technical quality of the building stones. 28 samples from the Sassi and Matera area have been analysed. By this means 6 different facies probably deposited in sea grass environments have been recognized. They are subdivided based on facies analysis and luminescence behavior. The first type is packstone to grainstone, containing macrofossils as pecten, ostracodes, benthic foraminifera, echinoderms, bivalve shells fragments, bryozoans and serpulids. Some bioclasts and cement show dark reddish to orange luminescence. The second type is a red algae rudstone with rhodoliths, planktic and benthic foraminifera, large mollusc shells, echinoderms and bryozoans. Cement shows bright orange to pink luminescence. The third type is a pack- to grainstone characterized by the presence of internal molds of large bivalves, abundant planktic foraminifera, mollusc shell fragments, benthic foraminifera, serpulids, echinoderms and barnacles. The fourth type is similar to the third one but is strongly cemented. Type five and six both represent lithoclastic calcarenite grainstones where the main difference is the grains size; type five is calcarenite and type six is a calcirudite. Both are very poorly cemented and contain clasts of reworked homogeneous and peloidal Cretaceous limestone, containing rudist fragments, dedolomite cristals, rare quarzitic rock fragments, and reddish to dark oxides. They show a bright luminescence in the thin crusts of syntaxial and micritic cement. In each type of the investigated calcarenite both inter- and intraparticle porosity is present. Syntaxial and micritic cement and rare dogthooth cement indicate crystallization in shallow marine or meteoric phreatic environments. These new detailed microfacies results of the Pleistocene calcarenite outcropping in Matera will be compared to those of the building stones in order to investigate if and how microfacies correlates with the degradation behaviour.

# Characterization of colorless topaz samples from Minas Gerais (Brazil) and Gilgit- Baltistan (Pakistan): a multi technical approach to highlight the different chemical and structural features

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Keywords: Topaz, multi technical approach.

In this work, a multi technical approach has been used to characterized Brazilian and Pakistan topaz samples through the use of spectroscopic and diffractionetric techniques in order to determine the possible evidence of different features between the two deposits. These clues could be useful to identify stones of unknown provenances. Gem-quality topaz, Al<sub>2</sub>SiO<sub>4</sub>(F,OH)<sub>2</sub>, is one of the most important F/OH-bearing silicates (Gatta et al., 2006), and crystallise in a granitic pegmatoid matrix or most in general it is associated to pneumatolithic/ hydrothermal events occurring in silicic igneous rocks (i.e., mostly granites and rhyolites). In particular, the most precious topaz gems come from Brazil, Russia, Japan and Pakistan and they are commercially known as top quality gems. Commonly, variously coloured topaz gems are widely used in jewellery, while colorless or light-blue stones have not relevant commercial value. The chemical characterization was carried out combining X-Ray Fluorescence (XRF), Scanning Electronic Microscopy (SEM-EDS) and Laser Ablation Inductively Coupled Plasma Mass (LA-ICP-MS) The obtained results highlight the main geochemical characteristics of analysed samples, in particular the high presence of metalloids (*i.e.*, Se, Ge, Ga) and Rear Earth Elements (REE) (i.e., Y). Raman spectroscopy, and. Afterwards, the samples have been characterized by X-ray powder diffraction. Specifically, the data were collected at the high resolution beamline ID22 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Cell parameters were calculated from X-ray diffraction data by means of the Rietveld method and fluorine content ( $w_{r}$ ) was estimated by a and b unitcell dimension. A critical correlation of the w<sub>E</sub> versus the refined lattice parameters and the known data allowed us to improve the regression lines for  $w_{F}$  versus a and b cell edges (Alberico et al., 2003). Finally, Raman spectroscopy allowed us to recognized the characteristic bands of the SiO<sub>4</sub> tetrahedra and Al-F stretching, the bending of SiO<sub>4</sub> tetrahedra and of Al<sub>2</sub>O<sub>3</sub> octahedra and also the OH<sup>-</sup> characteristic bands. Moreover, this technique enabled us to determine the nature of the solid inclusions present only in the Pakistan samples. To conclude, the chemical and structural data obtained by XRF, SEM-EDS, LA-ICP-MS, XRD and Raman techniques, document the occurrence of typical topaz patterns in spite of the different origin and composition of the host rock.

Alberico, A., Ferrando, S., Ivaldi, G., & Ferraris, G. (2003): X-ray single-crystal structure refinement of an OH-rich topaz from Sulu UHP terrane (Eastern China)-Structural foundation of the correlation between cell parameters and fluorine content. European Journal of Mineralogy, 15(5), 875-881.

Gatta, G.D., Nestola, F., Bromiley, G.D. & Loose, A. (2006): New insight into crystal chemistry of topaz: A multimethodological study. American Mineralogist, 91(11-12), 1839-1846.

### The informative exchange between documentary researches and instrumental investigations: an application for the protection of the graffiti plasters in Messina

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Keywords: analysis of materials, graffiti plasters, non-destructive tests.

It is a good rule for the restoration of any building - above all for those constituting the historical architectural heritage - undertaking a prior phase of knowledge that, in addition to retracing the building evolution from its origins to the actual state, is based on the so-called "analysis of materials". Indeed, a careful survey of the basic elements is unavoidable to investigate the technical-constructive aspects, which can be traced through the interpolation of data obtained, at the same time, from specific documentary resources and targeted diagnostic programs.

However, the research activity about the recurring use of the graffiti technique, and its variations, for the façade finishes of some buildings in Messina - erected after the earthquake of 1908 and attributed to the Florentine architect Gino Coppedè - has brought out both the difficulty of finding, in archival and bibliographic sources, the peculiarities of materials and executive modalities of the original decorative plasterworks, and the lack of attention paid to an in-depth knowledge in case of restoration. Especially in these cases it is important the synergy with the field of Geosciences because their skills and instruments allow, thanks to tests that can be little invasive, to reveal materials up to the microscopic level and to define the physico-chemical properties that determine their behaviour and compatibility.

Therefore, with the further intention to increase the knowledge of the technical culture of the first half of the 20th century, an investigation is proposed on the graffiti plasters of the façade second register of the Caseggiato Cerruti, built in the '20s in a sector of the block 319 of the Borzi Plan (the town planning implemented after the earthquake of 1908) and for which the documental research has given back incomplete results. The evident state of decay, which is unfortunately erasing a testimony of the historical architectural heritage of the city, has partially unveiled the stratigraphy allowing some reflections on the construction methods. In order to confirm the already formulated hypotheses, it is planned to examine in-depth the knowledge with the help of *in situ* non-destructive tests, relevant for the semi-quantitative chemical characterization of the mineralogical phases of the mortars employed for the decorative apparatus, with the aim to evaluate the number and the sequences of layers and the chromatic choices adopted.

In the development of the research topic, the need was felt to propose the addition of an attribute to the expression "analysis of materials" that emphasizes the importance of mutual informative exchange between documentary and instrumental evidences, desirable to achieve a greater level of knowledge of the building. Then, the "critical" analysis of materials and techniques used in the constructive tradition is configured as an instrument to launch more conscious actions to safeguard the architectural heritage and its historical memory.

### SmART scan procedure: an alternative to XRF-scanners?

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Keywords: XRF scanners, Handheld XRF/XRD mapping, portable XRD/XRF (Duetto).

XRF-scanners revolutionized the way paintings are analyzed. They produce outstanding results with unsurpassed resolution in mapping the distribution of pigments in a painting. Given their high cost, though, they are not accessible to every laboratory. As an alternative to the powerful XRD-scanners, a new procedure based on a reduced number of measurements obtained according to a grid or randomly selected by the operator, is presented. The measurements are interpolated using information contained in a high resolution visible image, while up to four other images can be simultaneously inserted in the process, giving further information. Smaller details of the object can be selected interactively, and different levels of resolution of the final map can be utilized to economize execution time. Generalized Procrustes Analysis and ad hoc data treatment are applied by the program. The algorithm that opt imizes the composition of each point in a maximum of fifteen dimensions will be discussed in detail. The composition information can be obtained by a hand-held XRF or by a portable XRD or Raman, on a grid of a selected number of rows and columns, or in a random manner, controlled by the operator. The researcher can apply his knowledge of the problem by selecting the points corresponding to each pigment in the whole palette. The false color maps produced show the distributions of each element/compounds over the entire surface of the painting. Up to 5 element files can be simultaneously read in, thus simulating compounds formulae. Several examples, such as mockups, Roman-Egyptian paintings compared with the results of an XRD-scanner, an XVI century painting possibly attributable to Rafael and a cross section of the Last Judgment by Michelangelo will be discussed in detail. One advantage of SmART scan over the XRF scanners is the possible use of techniques such as XRD and Raman, which directly give the maps of compounds rather than of elements. A second advantage is that, provided that the original researcher precisely indicated in the report the position of the point analysis together with the values of the measurements, one can even apply the procedure to analyses carried out several years before, as is the case of Michelangelo section analyzed by SEM-EDS in 1992. The results shown in this paper convinced us that, though not of the high level resolution of modern XRF scanners, this procedure can be of some help in the routine work of painting analysis. Its simplicity, low cost, the possibility to apply it retroactively, the real portability of the method that can be applied for example to mural paintings and the direct mapping of pigments make it a useful tool.

# The Deposition from the Cross in the Church of Saint-Germain-en-Laye (France): a masterpiece of Romanesque sculpture? Materials characterization to solve a 20<sup>th</sup> c. mystery

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Keywords: Raman spectroscopy, powder X-ray diffraction, PR49.

Dating and authenticating stone sculpted works of art is a challenging aspect of cultural heritage studies. In fact, it is possible to provenance the rock, by comparison of petrological, mineralogical and geochemical data, but no dating of the sculpture can be obtained. Also, stylistic observations need to be considered with care (Laruffa, 2006). However, in the case of mastic incrustation sculptures, the applied polychromy can support dating studies, based on pigments and binders.

In the church of Saint-Germain-en-Laye, a *haut-relief* representing the Deposition from the Cross is exposed (Birden, 2017). This sculpture resembles closely the Deposition from the Cross in the transept of Parma Cathedral, dated 1178 and "signed" by Benedetto Antelami. However, the St-Germain Deposition appeared in 1994, when it was donated to the parish by the descendants of Julian Duperrier, marble worker and collector of Italian antiquities. His last trip to Italy took place in 1924. No information is available on his deal, neither on the transport means arranged, nor on the sculpture itself (author, contractor, date, etc). The slab in *pietra d'Istria* is decorated with red and black mastics.

Art historical and historical considerations propose either a 12<sup>th</sup> or 19<sup>th</sup>-20<sup>th</sup> c. context for the creation of the sculpture (Méténier, 2018). Chemical analyses of the pigments and binders are therefore proposed to clarify the dating the work of art. Microscopic samples are characterized by a multi-analytical approach: vibrational spectroscopies and X-ray powder diffraction are used to characterize the rock and the polychrome mastic.

The rock is calcareous, and shows sulphation issues. Through Raman scattering measurements, the pigments were identified: carbon in the black mastic, and a mixture of red lead and a modern synthetic pigment (PR49) in the red areas. This information sheds new light on the chronology (Standeven, 2008) and manufacture of the Deposition from the Cross of Saint-Germain-en-Laye. These results allow for a better definition of further lines of research, in terms of chemical, historical and art historical interdisciplinary studies.

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# Mineralogical-compositional variations in the production technologies of mortars used in some Italian medieval fortifications located in different territorial and historical contexts

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Keywords: Binder, Aggregate, Medieval fortification.

The goal of research is the mineralogical-petrographic study of the mortars used in some medieval fortification walls of XVI century located in the Siena and Cagliari cities. In the first case, the mortars of the walls designed by Baldassarre Peruzzi were studied, while in the second case the mortars used in the Santa Croce's walls (within the "Castello" district) were studied. From the beginning of the sixteenth century until the end of XVI and the XVII centuries, these two ancient fortifications were affected by different masonry transformations, which resulted in different mortar types. The compositional characterization of the entrapment mortars of the historical buildings can be a particularly significant tool for: i) the definition of the construction phases of a ancient yard site and its transformations over time, ii) the realization of data-base timescales valid for local level but also on a national scale, iii) the possible identification, in a synchronic dimension, of mortars selected for specific building types. Therefore, the final purpose of the research is to compare the mortars of the XVI century with those used in the wall circles dating back to previous periods (XIV and XV century) and located in different Italian territories (i.e., Tuscany and Sardinia), to understand the variations of the processing technologies of the raw materials for the production of the mortars.

The research at the moment focuses attention on the entrapment mortars of brick walls taken from different portions in Peruzzian walls of the Siena fortifications. The samples were chosen according to their representativeness but above all on the basis of the chronological significance. Preliminary investigations have highlighted the use of different types of mortar compared to previous ones, characterized by high hydraulicity indexes and a greater care in the selection and treatment of raw materials for the aggregates. In fact, the mortars show a narrow dimensional distribution of aggregate (referable to a use of sands with a grain size from very fine to fine) and the little presence of silty or coarser components. Among the constituents of the aggregate are mainly quartz granules (both in monocrystals and in polycrystalline aggregates), belonging to the typical Pliocene marine sands on which the historical centre of Siena is located. The binding / aggregate ratios are usually higher (1/1) in mortars of the sixteenth century compared to mortar three-fifteenth century (around 1/2).

These evidences, taken from the compositional point of view, between the mortars of the XIV and those of the following centuries suggest a deliberate choice of new materials, more technologically advanced, in the context of major upgrades to the city defenses implemented at the beginning of the sixteenth century.

# Iron age black glass from Italy and Slovakia: technological evolution of early natron glass vs wood ash technology

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Keywords: archaeometry, black glass, Iron Age.

Recent studies on Iron Age (10th-8th cent BC) black glasses found in France (Gratuze & Picon, 2006) and Jordan (Reade et al., 2009) demonstrated that they were among the first natron glass varieties ever produced. All these samples share the same chemical features: low K<sub>2</sub>O and MgO, very high FeO and low CaO. Consistently, (E)SEM-EDS analyses evidenced the presence of many unmelted grains of heavy minerals (e.g. chromite, iron oxides). The present study aims to investigate the chemical-physical features of 96 Iron Age black glass beads dated to the 9th-5th cent BC coming from Torre Galli, Francavilla Marittima, Cumae, Pozzuoli, Sarno and Bologna (Italy), and Chotin (Slovakia). SEM-EDS, EMPA, and LA-ICPMS analyses -as well as that of Sr and Nd isotopes performed on a selection of samples- provided evidences for different production technologies. The black samples recovered in Italy are all natron-based glass probably produced in Egypt, but they can be divided into two groups characterized by the use of different silica sources and recipes. In fact, the oldest samples (9<sup>th</sup>-8<sup>th</sup> cent. BC) were produced from very impure iron-rich sands directly mixed with natron, while the more recent ones (7th-6th cent. BC) were made from mature sands - generally used for high-quality natron-based glass - and then colored by the addition of iron oxides. The oldest samples fit therefore the picture for the earliest natron black glass produced with impure sands also found in France and Jordan. Conversely, the more recent samples (7th-6th cent. BC) indicate a technological refinement in the production of the natron glass during the 1<sup>st</sup> millennium BC. In these latter samples, the choice of mineralogically mature sands with CaO contents high enough to stabilize the glass allowed the production of high-quality glass colored in different nuances, which will be the technology employed during the subsequent Roman period. The Chotin samples dated to the 5<sup>th</sup> cent BC, appear very different from the Italian ones, being characterised by low Na<sub>2</sub>O, but high K<sub>2</sub>O, CaO and P<sub>2</sub>O<sub>5</sub>, which suggest that wood ash was used as a flux. The colouring technique employed, instead, was the same used for the oldest natron black glass, that is the intentional choice of dark sands. The Chotin wood ash glass has no equivalent among its coeval glass chemical typologies, exhibiting a great affinity with the 'Early Wood Ash Glass' produced in central Europe during the Medieval period.

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# Application of vibrational spectroscopy and X-Ray Diffraction to the study of building materials from the Exedra of S. Nicolò l'Arena in Catania (Italy)

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Keywords: Plaster, Siracusa stone, Etnean lava.

The Exedra of S. Nicolò l'Arena in Catania (Italy) is a tripartite two-levels structure built up in 1722 in front of the homonymous Monastery. The Exedra façade is composed by natural and artificial stone materials such as *Siracusa stone* used to realize portals and windows frames, and Etnean lava, employed for the basement. All plane surfaces of the Exedra were coated with a reddish plaster whose color is due to the presence of the so-called "ghiara" or "rena rossa" (a reddish sediment modified by contact with lava) in the surface finishing mixture, a typical feature of Catania historic buildings, especially after 1850.

Natural and artificial stone materials were characterized by means of vibrational spectroscopic methods such as Raman and FTIR-ATR spectroscopy and by XRD in order to get more precise information about the *rena rossa* surface finishing mineralogical compositions and secondary phases due to aerial deposition and/or alteration phenomena

Here a multi-technique study focused on the central building façade is presented with the aim of both describing the peculiar features of the structure and materials, and evidencing alteration processes affecting them. The spectroscopic and XRD analyses revealed the diffuse presence of gypsum and calcium oxalates, together with that of amorphous silica-based compounds and elemental sulfur (referable to effusive activity of the near Etna volcano).

The detailed examination of plasters surfaces, as well as of their inner and back layers, exhibited compositions compatible with historical recipes and local building materials, in particular the employment of a lime-gypsum mixed binder, because of comparable intensity shown by calcite and gypsum Raman features; parallel also sulfation phenomena affecting the whole volume of collected samples were observed. Surfaces covered by the *ghiara*-based finishing layer showed, in addition to main component calcite (lime), also hematite and clayminerals belonging to the *ghiara*; other phases, due both to typical *rena rossa* composition and to volcanic ashes deposits on the plasters surfaces, were also identified, such as pyroxenes, K-feldspars, magnetite, and magnesioferrite.

#### Characterization of Roman glass from Casa Bacco deposit at Pompeii

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Keywords: Roman glass, Pompeii, Production technologies.

A set of 15 intensely colored and variously decorated Roman glass coming from Casa Bacco deposit at Pompeii were investigated. The objects analyzed are glassware including cups, jars, bottles and plates and one raw glass chunk with a wide color range (colorless, green, blue, yellow). Two glass samples are characterized by a decoration on the surface: a yellow bird-shaped ampoule with a metallic effect coating and a blue glass jar with a white decoration. The glass fragments were chemically characterized by wavelength-dispersive electron probe microanalysis (EPMA) aimed to identify the raw materials and production technologies employed in the manufacture of the glassware. The achieved results, compared with literature data (Silvestri et al., 2005; 2008; Silvestri, 2008; Gallo et al. 2013), highlighted that the most of the analyzed Pompeii glasses has the typical composition of the Roman glass, produced with the natron as flux and the manganese as decoloring agent. The chemical composition of some green glass, may be ascribed to the use of plant ash rather than natron and/or to the recycling of alkali rich glass scraps, considering the high tin and lead contents too. The blue glasses were produced using a Co-Cu bearing minerals as coloring agent (probably trianite), while copper and iron are responsible of the yellow glass color. The micro-structural analysis on the two decorated glasses has highlighted the use of specialized technology by Roman glassmakers to produce refined objects. In the tiny bird-shaped ampoule the analysis has shown a very fine metallic coating with high tin concentration. The white decoration of the blue glass jar contains numerous and dispersed Sb-Ca rich crystals, suggesting the use of antimony oxide as opacifier agent.

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### Geochemical, mineralogical and petrographic study of the natural and artificial stone materials from the Monasterace Castle (Calabria- Southern Italy)

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Keywords: archaeometry, mortars, plasters.

This work shows the results of the archaeometric study performed on 20 samples coming from the masonry structures of the Monasterace Castle, located along the Ionian coast of Calabria (Southern Italy). The castle, visible in the upper part of the Monasterace village, dates back, in its current form of fortress-palace, to the end of the 16th - beginning of the 17th century (de Nittis, 2016; Martorano, 2017). From the different floors of the Castle were collected stone materials, mortar and plaster samples that were studied through a methodological approach based on the application of different analytical techniques such as Optical Microscopy (OM), X-ray Powder Diffraction (XRPD), Electron Probe Micro Analysis (EPMA) and Raman Spectroscopy, finalized to the petrographic, mineralogical and geochemical characterization of the samples. Data produced provided us a complete characterization of the samples to use for planning new restoration works and allowed us to obtain information about the building techniques and the constructive history of the Castle. The raw materials identified, employed for the construction of the building, are partially compatible with the geology of the area, as already demonstrated by a previous study performed by Miriello & De Luca (2016) on plasters coming from the Castle. At the same time, the discovery of slate and Neapolitan yellow tuff allowed us to hypothesize the importation of stone materials from different areas. Furthermore, the study of the binder of the mortar and plaster samples highlighted the use of lime coming from the cooking of magnesian limestone, visible also in other Calabrian buildings (De Luca et al., 2016).

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### The decline of the Nasca culture (Peru) as the result of an increasing environmental stress: overcoming the paradigm formulated at Cahuachi of catastrophic mega-floods due to El Niño-Southern Oscillation

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Keywords: Geoarchaeology, archaeometry, Nasca culture.

Cahuachi, located on the coastal desert of Southern Peru (Nasca Province), represented the main ceremonial site centre of the Nasca culture. An hypothesis of destruction of the site related to catastrophic floods (the youngest around the 10<sup>th</sup> century AD), due to El Niño-Southern Oscillation (ENSO) was proposed by Grodzicki three decades ago. This paradigm finally led to believe that Cahuachi was covered by huge floods accumulating conglomerates up to the top of the highest buildings. By contrast archaeological evidence in the Nasca Phase IV period emphasizes a high-magnitude earthquake and two moderate-to-major, non-catastrophic floods between 400 and 450 AD, leading to the progressive abandonment of large areas of the ceremonial centre.

To test the above hypothesis, a stratigraphic succession outcropping on the bedrock of the "Pirámide Sur" at Cahuachi was investigated by means of mineralogy, petrography and sedimentology. The succession consists of mudstones, siltstones, sandstones and conglomerates, all sharing similar silty-clayey components. Conglomerates, likely resulting from progradation of alluvial fan systems, have the same lithotypes of pebbles. In addition, the conglomerates occurring at the top of the section unequivocally underlie the ceremonial buildings. It is worth to note, the surveyed stratigraphic section well correlates with the Upper Pliocene-Lower Pleistocene "Changuillo Formation". This finding is at odd with the late Holocene age proposed by Grodzicki for this succession. However, the hydrogeological hazard assessed at Cahuachi (the occurrence of *huaycos* i.e. debris flows triggered by extreme rain events) and intense periods of earthquake activity are consistent with the progressive influence of destructive natural events on the decline of the Nasca culture. We thus analysed the ENSO cycle in the Peru margin, to check the possible correlation of times of more intense activity with the period of the Cahuachi and Nasca cultures decline.

As the rainfalls in the western Pacific and the eastern and mid Pacific are closely related to the Southern Oscillation Index (SOI) the apparent increase of this latter from 200 to 700 AD, might be closely associated to a strengthen of La Niña events (wet condition), with a period of environmental crisis leading to several moderate-major *huaycos* rather than catastrophic floods. In addition, based on criteria and data available from the National Geophysical Data Center, NOAA, an earthquake of magnitude similar to one of the nine most significant of the area in the last six centuries, hit Cahuachi during Phase IV. We suggest, that, rather than the mere effect of ENSO-related catastrophic floods, the decline of Cahuachi was related to a complex succession of natural disaster events. A progressive weakness of the resiliency of the Cahuachi population, coupled with possible changes in social acceptance of the environmental stress as motivated by the religious hierarchy, will be unraveled.

#### Compositional fingerprints of primary and secondary chert sources in Northern Apulia

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Keywords: Chert, Neolithic, Tavoliere.

Northern Apulia played a key role in Neolitisation of Western Europe. The Tavoliere plain was extensively anthropised in the Neolithic as a ideal place for agriculture and breeding, The Gargano promontory, mainly on the eastern part, provides several outcrops of primary, sub-primary and secondary chert sources, as well as a secondary sources of knappable materials were directly available in the marine and fluvial terraces. In the north-eastern part of the Gargano promontory at least 20 mining sites were active from the early Neolithic to the early Bronze Age. The remarkable mining network attests the great quantity and quality of chert-bearing rock types: more specifically, three Gargano formations were mined: Peschici limestone, Scaglia and Maiolica formations.

Our recent investigation of the secondary chert sources in northern Apulia allow us to trace out the main differences from a petrographical and geochemical point of view, and to provide a GIS-based geological map of the primary and secondary chert sources.

The macroscopic, stereoscopic and chemical (pED-XRF) analysis of a selection of 164 samples of chert from ten Neolithic mining districts and geological outcrops throughout Gargano Promontory (primary sources) and 50 samples of siliceous pebbles collected in the coastal deposits nearby Mattinata and Siponto (secondary sources) and in the alluvial and marine terraces of Tavoliere Plain (94) provided a reference dataset to compare with the data obtained on chert tools and débitage from Neolithic excavated contexts in Apulia, aimed to locate their provenance.

A cluster analysis procedure was chosen in order to classify studied objects after a mixed data matrix and implement provenance study. A total of thirty-six variables (structure, texture and fracture features, three colour coordinates and eleven chemical element concentrations, six microfossils observations) was handled for 308 samples. Partitional clustering algorithm PAM gives back groups of more similar object. Primary sources are distributed in three groups, one include Maiolica and Scaglia mines and two groups contain Peschici limestone mines. Secondary sources of Mattinata and Siponto partially overlap with Maiolica samples. The secondary chert from Tavoliere Plain has distinctive compositional fingerprints attributable to southern Apennines origin.

### New data on the vitreous inlay of the "Marmi Mischi" baroque decorations from the Messina regional museum (Sicily, Italy)

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Keywords: mixed marbles, glass decorations, raw materials.

"Marmi mischi" (mixed marbles) are artificial Ca-rich glass decorations used in Sicily during Baroque, to adorn wall and altar. They are known as "vetri di carcara" and were obtained by burning in specific furnaces (carcara) of limestones, marly limestones or dolomitic limestones, to obtain CaO. After roasting of the carbonatic rocks, the glassy to vitreous materials found at the bottom of the ancient limekilns as a secondary product of the lime production, mostly green-blue coloured, was collected and used as "mischi" glass decorations (Montana and Gagliardo Briuccia, 1998). Similar Ca-rich glassy materials from the "Fiore Deposit" have been already studied by Triscari et al. (2009) to carry out informations about colour origin. Another study by Artioli et al. (2009) characterized similar Baroque glass decorations from Palermo Churches and defined them as carcara glasses.

In this study we provide information on the used raw materials and pigments used for glassy decorations of an altar frontal (Pallium altaris) from the Messina Regional Museum. To reach this objective, glass decorations have been analysed by means of portable X-Ray Fluorescence through in situ not destructive analyses.

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Triscari, M., Sabatino, G., Giuliano, A. (2009): The colour origin in the vitreous inlay of the "marmi mischi" Baroque decorations. AIAR, Ravenna.

#### Archaeometric studies on the wall paintings of the St. Maria Veterana archaeological site in Triggiano (Bari, Italy)

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Keywords: archaeometry, wall paintings, Apulia.

This study focussed on the wall paintings of the archaeological site of the St. Maria Veterana's church (Triggiano, Bari) and aimed to contribute, by means of archaeometric investigation, to the knowledge and historical hypothesis about the church and the development of this Apulia small town.

The St. Maria Veterana's church was found in the 11<sup>th</sup> century by a rich priest outside the walls and near a moat that already in the 10<sup>th</sup> century housed the first settlement of Triggiano. Contrarily to the pre-existing cave churches, this building was a masonry basilica with three naves and appeared completely painted as proved by pictorial remains, sometimes multi-layered, on side walls and on the pillars. In the second half of the 15<sup>th</sup> century, an exceptional population increase and a modernization of the inhabited centre occurred until the end of the 16<sup>th</sup> century, when the medieval church was literally cut, filled with its own ruins and a new church was built above (Battista, 1983). The underground site remained hidden and unknown until, in the '80s of the last century, archaeological excavations and restoration programs were carried out.

The sample collection involved about 30 micro-fragments of wall paintings from different areas of the basilica, including supports and pictorial layers. Firstly, samples were observed by stereomicroscope and detailed description and photographic documentation were recorded. Afterward, the most representative fragments were inserted in epoxy resin, abraded and polished to analysing samples in cross-sections by means of a reflected-light optical microscope, in order to obtain information regarding features of painting layers (e.g. stratigraphy, number and thickness of painting layers, type and pigment abundance).

For some samples, thin sections were prepared and observed by polarized-light microscope, focussing on textural and petrographic characteristics of the painting supports.

Some of remaining samples were investigated by powder X-ray diffractometer, to obtain information on the mineralogical composition of used materials. Moreover, additional data in terms of morphology and chemical composition of pictorial layers were achieved through scanning electron microscope equipped with X-ray microanalysis.

The archaeometric results allowed to know the features of raw materials, the execution techniques and the conservation state of the wall paintings. The data crossing and their comparison with the historical hypothesis provided valuable information about the building phases and the attendance of the basilica in time.

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#### Conservation and maintenance of the ornamental stones in the city of Torino: focus on graffiti vandalism

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Keywords: conservation, ornamental stones, graffiti vandalism.

The field of the conservation of ornamental stones and architecture heritage is a particular branch of the Science of Cultural Heritage that usually concerns large surfaces, with both structural and ornamental function and placed in external environment. Against this background a research project regarding the conservation of historical architecture, urban and cultural heritage and in particular regarding cleaning and protection of ornamental stones from graffiti vandalism was developed.

In this context, the role of Geosciences is fundamental in order to characterize these ornamental stones and to support a correct diagnosis of conservation state. In this research project, the case study of Torino, which shows an extraordinary richness in terms of variety of ornamental stones, was considered; in fact, more than 50 different lithotypes are employed in the Historical and Modern Architecture Heritage. This richness in materials is certainly due to the varied geological nature of Piemonte region (Borghi et al., 2013).

The first phase of the project consisted in a site survey performed in the city centre, mapping the most employed ornamental stones and graffiti materials and colours. Thanks to this survey it was possible to select the materials to be considered in the study (stone materials, graffiti paints and anti-graffiti products) and the preparation of a set of stone specimens. Therefore, based on their abundance and different characteristics, five different lithotypes, six different graffiti paints and colours and finally, both sacrificial and permanent anti-graffiti products were selected. A multi-analytical protocol was set-up and applied on these rock samples: both invasive and non-invasive techniques were performed in order to evaluate and compare the effectiveness and harmfulness of different cleaning and protection treatments (Sanmartin P et al., 2014). An overview about lithotypes employed as ornamental stones in the city of Turin will be presented, as well as the petrographic characterization of the selected ones. It will be discussed the application of this protocol as example of analytical methods focused on generating data useful for the output of research: the application in a real urban context and design of useful guidelines for a correct maintenance of ornamental stones in architecture heritage.

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# The Mediterranean trading centre of Vivara (southern Italy): new insights on the production and circulation of pottery during the Bronze Age (XVI -XV century B.C.)

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Keywords: Bronze Age pottery, ceramic technology, Vivara.

The island of Vivara represented an important Mediterranean trading center during the Bronze Age due to its strategic geographic position. Besides being an important venue of Greek trades involving long-distance operating merchants from western and eastern Mediterranean Sea, it was particularly flourishing for the commerce of metals, mainly come from the Central Italy, where metal reserves were located.

Along with the metallurgic industry, it was attested the development of ceramic production, both reflecting the local and eastern material culture. New insights on the ceramic production of Vivara were provided by recent researches performed in 2016 in the western part of the island, in the site of Punta D'Alaca. A Bronze Age thriving settlement was here unearthed, whose archaeological evidences highlighted that, alongside a profitable business relationship with Mycenaean traders, skillful Aegean artisans developed a more accurate ceramic production adopting local raw materials and new technological choices (e.g. use of wheel), different from the local artisanal practices (handmade coarse vessels).

Many of this type of artifacts were recovered in the archaeological records; twenty representative samples of common wares, constituted by *ollae*, bowls, *dolii*, *pithos* and jugs, were collected for archaeometric analyses (OM, SEM-EDS, FTIR, XRPD) in order to determine technology and provenance.

Archaeometric analyses highlighted the occurrence of two group samples; the main group is constituted by specimens characterised by the occurrence of volcanic temper scattered in low-CaO clayey matrices. The presence of sanidine, diopside, juveniles, plagioclase, micas and rare Fo-olivine attested the local provenance of temper, compositionally consistent with the volcanic products of Procida. Regarding the technology, the rough conditions in which the artifacts were fired brought about variable firing temperatures. FTIR and XRPD analyses, in fact, revealed, in some samples, the presence of detectable clay minerals (interstratified clays, kaolinite, chlorite) along with residual illite-like phases suggesting rather low equivalent firing temperatures ( $\leq$  ca. 500 °C). On the other hand, when they lack and only residual illite/mica persists, higher firing temperatures can be supposed.

The second group is formed by three samples that differ from the local-manufactured vessels due to their mineralogical and textural features. Actually, two samples were characterised by quartz feldspar, rare clinopyroxene and scoriae as temper-grains whereas one sample showed orthoclase, microcline, polimineralic aggregates of quartz and micas and tourmaline as coarser particles. If for two samples key-elements for the determination of provenance were not clearly identified, in the *olla* containing tourmaline (classified as schorl and dravite) the provenance was constrained to the Gavorrano area in southern Tuscany.

### Multi-analytical study of the triptych by Tino di Camaino of the Monte dei Paschi Bank collection in Siena (Italy)

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Keywords: Medieval Sienese sculpture, Optical microscopy, Digital 3D microscopy.

Tino di Camaino was a fourteenth century Sienese sculptor, who executed his artworks (mainly sepulchral monuments) in Siena, Pisa, Florence and Naples. The Monte dei Paschi Bank in Siena bought a marble triptych by Tino in the late 1980s. The triptych represents the Virgin Mary with Jesus and the Saints Catherine of Alexandria and John the Baptist. The date of execution of the triptych was in the 1330s, when Tino was in Naples. At the end of the nineteenth century the sculpture was divided into two parts, one of which is held by the Monte dei Paschi Bank, and the other one is a part of the Salini collection, near Siena.

The triptych is carved on marble and has rare traces of pigments and mortars (on the edges).

A multi-analytical study of the triptych was carried out, aimed at characterizing the materials (stone, mortars and pigments) and identifying the sculptural techniques.

Micro-invasive and non-invasive methods were used. Non-invasive analyses were carried out by means of a digital 3D KH 7700 Hirox microscope, which allows obtaining detailed micro-morphological three-dimensional colour images of surfaces, with the possibility to carry out linear and angular x, y, z measurements. Few micro-samples, smaller than 1 mm<sup>3</sup>, were taken. Ultra-thin sections, having thickness lower than 10  $\mu$ m, cut perpendicularly to the surface of the sample, were obtained from the micro-fragments. These sections are fundamental for the observation of micro-cryptocrystalline aggregates under the polarized light microscope (Leica DMRXP).

The ultra-thin sections were analyzed also by means of X-ray diffraction (XRD). A x-ray diffractometer (Philips X'Pert PRO PW 3040 with X'Celerator PW 3015 detector) equipped with a mono-capillary collimator tube was used. This instrument allows investigating very small samples and/or elliptical areas with minor axis lenght of 100  $\mu$ m.

A scanning electron microscope (Philips XL30) equipped with an energy dispersive microanalytical system EDAX-DX4 (SEM-EDS) was used for chemical analysis.

The most significant results were the identification of the marble and mortars' provenance, the characterization of pigments and products of past restoration interventions and the identification of the tools and techniques used to carry out the triptych.

The marble of the artwork shows a seriate-interlobate microstructure. The macro and microscopic observations allowed to exclude the use of a local Montagnola Senese marble and to hypothesize a provenance of the marble from the Apuan Alps, in particular from the western sector of the ridge (e.g. Carrara marble).

The mortars at the edges of the sculpture are lime mortars containing aggregates of glass fragments deriving from volcanic products. These kinds of mortars, never found in artworks or monuments in the Sienese territory, can be quite common in Naples. Therefore the evidence is consistent with a manufacture of the sculpture in Naples.

Azurite, lead white and barium sulfate are present in the background of the Saints, while lead white and ochres applied with an organic binder (mission for gilding) were found on the leafs of the tympana.

The traces left by the tools for marble carving testify the use of different types of instruments, like chisel, compass and drill. The information collected represents a first set of data useful for the creation of a database of tools used by Tino di Camaino and to shed light on his sculptural technique.

#### Historic mortar recipes at Palermo from the roman age up to the late modern period: knowledge for local restoration practice

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Keywords: historic mortars, Palermo, Sicily.

Over a period of more than twenty years, almost 200 samples consisting of lime-based and hydraulic mortars collected from many different archaeological sites and monumental buildings of Palermo, have been characterized by means of mineralogical-petrographic techniques. The considered samples reflect different end-uses (plastering, flooring, binding) and cover an extremely wide chronological range, from the Hellenistic-Roman age to the Art Nouveau period. The adopted techniques were mostly thin-section microscopy, X-ray powder diffraction analysis and scanning electron microscopy coupled with qualitative and quantitative energy dispersive spectrometry.

The mineralogical and petrographic investigations, carried out within several case studies, allowed to ascertain different recipes used in terms of both compositional and textural features. The present contribution is thus aimed to a comparative evaluation of the different recipes in terms of frequency, functionality and temporal persistence.

Aerial lime based binders (more often magnesium-bearing) and different proportions of alluvial calcareous and siliceous sands most frequently characterize the diachronically adopted recipes, interchangeably used for wall coatings and decorations. The use of hydraulic mortars (with variable proportions of *pozzolana* and/ or *cocciopesto*) was mainly documented for floor covering specially during the Roman age. The mortars of the Arab-Norman period (well documented at the Royal Palace) are characterized in a peculiar way by the presence of sand aggregate artificially produced by crushing the local biocalcarenite, as evidence of the use of stone masonry scraps. For over five centuries (from the 14th century until the first half of the 20th century) the sand for the preparation of mortars in Palermo was taken from the sea near the mouth of the small rivers. It was the hard job of the *saurrieri* (sand digger). The sand was taken in the shallow sea, sailing along the coast between the localities *Bandita* and *Sperone* because in those places there was the best quality sand made of smooth and rounded grains of quartz and flint rather than calcareous shells fragments (that mix badly with aerial lime). A surprising continuity both in the selection criteria of raw materials and in the formulation of the specific recipes was established. Only through the systematic study of the ancient recipes it will be possible to formulate restoration mortars with full awareness.

## The role of Geoscience in the diagnostic, conservation and valorization of underwater cultural heritage: examples of National and European projects

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Keywords: Geoscience, underwater, Cultural Heritage.

In recent decades, following the UNESCO 2001. Convention on the Protection of the Underwater Cultural Heritage, there has been an increasing interest in the preservation and management of the submerged heritage. As known, in fact, the marine environment promotes the development of deterioration phenomena on submerged archaeological structures, such as biological colonization by organisms, ionic corrosion and oxidation, which, sometimes, can cause serious alteration. In particular, the deterioration of natural and artificial stone materials is related to several factors associated to their intrinsic characteristics, such as texture, composition, technological properties, porosity, hardness and strength, as well as to the environmental conditions they are exposed to. Some important advances have been reached in this research field and the high reactivity of materials against the chemical and mechanical alteration is well known.

In this framework, various researches funded by several National and European projects will be presented. In particular, the data arising from COMAS project (COnservazione programmata in situ, dei Manufatti Archeologici Sommersi) concerning the study of degradation and alteration phenomena in the underwater environment will be exposed. They regarded characterization and in situ experimental testing of new nanomaterials on marbles and bricks of the archaeological site of Baia (Naples, Italy). With regard to the mortars used in the underwater environment, the preliminary results of MaTACoS (Materiali e Tecnologie avanzate Applicate alla Conservazione Subacquea) project (still in progress), funded by MISE - Ministero per lo Sviluppo Economico, will be introduced.

At the same time, the results of the BLUEMED Project, funded by the European Interreg MED Programme, concerning the identification and testing of new methods for providing public access and managing Underwater Cultural Heritage sites will be discussed as well as preliminary results of MAGNA project (On the Route from Greece to Magna Grecia) funded by EASME - Executive Agency for SMEs about the issue of the valorization of Underwater Cultural Heritage.

#### Petrographic study of the Bronze Age ceramics from Shahr-I Sokhta in east of Iran

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Keywords: ceramic, XRF, SEM-EDX.

The Shahr-i Sokhta (The Burnt City) is a Bronze Age archaeological site in east of Iran with several stages of settlements. A large number of pottery shred and excavated ceramics of this site shows its importance during fourth to second millennium BC. Based on the color of body-paste of found ceramics in Shahr-i Sokhta, they are classified into three "Red", "Grey" and "Buff" ware groups. An analysis of the microstructure and chemical composition of these three groups is the main purpose of this study. To do so, nine samples (three for each group) were subjected to observation by optical microscope and then their thin sections were analyzed by PLM, micro XRF and SEM-EDX to investigate any differences of raw materials from which these ceramics were produced. The results demonstrated that both Red and Grey ware ceramics have similar compositions with high amount of Fe and difference of their color is most probably because of different kiln atmosphere in which the potteries were produced. On the other hand, the high percentage of Ca in the Buff ware samples showed this type of ceramics are made with another type of raw material; different source or prepared deliberately. Moreover, PLM and SEM studies illustrated there wasn't any cover layer on these ceramics, and, a paste with fine particles created all the bodies. Also, the percentage of organic additions shamot in the body of Grey and Buff samples are low while in the Red ware ceramics it is totally absent.

## Authentication study of majolicas from the *Museo Nazionale del Bargello*, Florence (Italy): the contribution of archaeometric analysis

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Keywords: authentication, majolica.

The *Museo Nazionale del Bargello* of Florence (Italy) has a remarkable collection of medieval and Renaissance majolicas. As in most museums originated in the 19<sup>th</sup> century, some of the museum objects entered the collection after the donation or acquisition of private collections, so that their original provenance is not documented. The main objective of this study is to determine whether some majolica items of the Bargello are genuine ancient artefacts or forgeries made between the end of the 19<sup>th</sup> and the beginning of the 20<sup>th</sup> century. Indeed, this period was characterized by new exciting archaeological discoveries and, inevitably, by an exceptional development of both the antique market and the production of forgeries.

The study of the style, iconography, acquisition history and condition of the Bargello majolicas lead the curators of the museum to question the authenticity of some of the objects historically catalogued as ancient. A multi-analytical archaeometric campaign was conducted to support these observations with objective data on the materials used. Three sets of glazed earthenware were studied: 14<sup>th</sup>-century (?) majolicas from Orvieto; 15<sup>th</sup>-century (?) majolicas from Deruta (Perugia); 15<sup>th</sup>-century (?) majolicas with lustred decorations.

The main technique used for pottery authentication certainly is thermoluminescence (TL) analysis (Craddock, 2009): this analysis was successfully performed through the CHNet-INFN facilities (<u>http://chnet.infn.it/it/</u>). However, we were also interested in *1*) increasing our knowledge on the materials and technology used for the production of majolicas both in ancient and modern times and *2*) developing a non-invasive authentication methodology (which is not the case of TL). For point *1*), we made cross sections of the objects and analysed them by optical and electron microscopy, in order to morphologically and compositionally characterize the stratigraphies and identify possible differences between ancient and modern objects. Artefacts with an appearance similar to the majolicas to be authenticated - both from documented archaeological excavations and of declared modern production - were also analysed for comparison. This was particularly important with regards to the modern objects, since archaeometric studies on  $19^{th}/20^{th}$  pottery are not abundant. Specific attention was given to the most superficial layers, i.e. the glaze and the lustre, and particularly to the pigments employed. For point *2*), the portable XRF spectrometer developed by CHNet-INFN (Florence) was used to analyse the glazed surfaces of the majolicas to be authenticated. The best working conditions for a non-invasive, *in-situ* analysis were determined and it was possible to detect the elements constituting the glaze and lustre decorations.

Craddock, P. (2009): Scientific investigation of copies, fakes and forgeries. Elsevier, Oxford.

#### Maiki Survey Project: archaeometrical analysis of pottery production in the Kurdistan Region

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Keywords: pottery, archaeometry, Kurdistan Region.

Sapienza University of Rome and the Department of Antiquities of Sulaimaniyah carried out an Archaeological Mission in the Iraqi Kurdistan (MAIKI) in order to study the historical, linguistic and cultural development of the Kurdish region.

This paper presents a study on the pottery materials collected during the surveys carried out by MAIKI, an area of approximately 850 km<sup>2</sup> located between the valleys of the rivers Basra and Dyala, along the road connecting the cities of Darbandikhan and Chamchamal.

Specific and updated studies on post-Assyrian pottery from the Kurdistan region are scanty. In turn, investigations on ceramic productions of this period and comparisons with those from the surrounding areas are very useful and deserve to be analysed.

The pottery corpus collected during the surveys is heterogeneous; it consists of ceramics related to a wide range of productions and a wide time span, from the Uruk-Jemdet Nasr period (3100-2900 BC) up to the Ottoman period (from 13<sup>th</sup> to 19<sup>th</sup> century).

Thereby, we adopted a specific methodology to in-depth characterise typological, compositional and discriminating attributes of the ceramic materials. The analyses were done using XRPD, OM, SEM-EDS and textural image analysis. These data allowed us to characterise and define the composition of the most important phases characterising the petro-fabrics into pottery assemblages, such to unveil new aspects concerning technology and production of the identified wares.

Matching quantitative results and information from the surveyed sites led us to outline a general frame of a local pottery productions reaching a good technological level; moreover, we also recognised some imported products.

# Tempering with white marbles: implications on the provenance and production technology of ancient pottery

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Keywords: temper, white marbles, petrography, O and C isotope analysis.

The addition of temper in the pottery production is attested since prehistoric times and is still a production choice adopted in modern ceramic industry. The type of temper comprises natural lithic materials (such as sand and rock fragments), materials of organic origin (vegetal or animal), as well as artificial products like grog/ chamotte (pottery fragments). When the temper is composed of minerals and rocks available in the area of the production site, they can be considered as useful markers to trace the provenance of pottery. On the contrary, the occurrence of different rock types outcropping in two or more geological areas far away each other, open new questions on the production technology. In fact, such situations can be explained only considering the recycling of imported rocks, including those used for architectonic elements or sculptures, mainly coming from buildings of previous epochs.

This study presents the evidence of the deliberate addition of recycled white marbles on a long term production (4th and 14th century AD) of coarse and cooking ware in north-eastern Italy. The petrographic analysis of about 200 potsherds, attested the use of this unusual kind of temper, on about half of the repertoire. The occurrence of different type of marbles, associated to rocks and minerals typical of the alluvial deposits of the eastern Po plain as well to locally available rocks (Euganean Hills trachyte), clearly pointed out the intentional addition of recycled marble fragments, and allow to exclude that the pottery was imported from other regions. Detailed petrographic analysis on the microstructure, maximum grain size (MGS), accessory minerals (when observed) and grain boundary shapes, allowed to constrain to the most important Mediterranean classical sources area Aegean the provenance of the marbles. These data were also partially confirmed by the stable oxygen and carbon isotope analysis on marble fragments mechanically separated from the ceramic paste. Nevertheless, part of the marble fragments were characterised by very negative  $\delta 13C$  values, not consistent with any marble variety. A series of firing experiment on two marbles were carried out in the temperature interval between 600°C and 800°C, both reproducing oxidising and reducing conditions, to evaluate whether these anomalous  $\delta 13C$  values could be related to the firing process.

#### Northern Black Polished (NBP) Ware from Barikot (north-western Pakistan): an archaeometric study

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Keywords: pottery, chemistry, mineralogy.

The northern black polished (NBP) ware resents a luxury ceramic class, dated to the Iron Age culture, attested in the Indian subcontinent and characterised by a black slip. It developed simultaneously to the growth of large urban centres.

The archaeometric analysis of a set of ten potsherds of NBP ware, dated between the III-II century BCE and the I century CE, found at the site of Barikot (Swat Valley, north-western Pakistan), was addressed to define the provenance of this pottery and to constrain the production technology of both the ceramic body and the black slip in terms of raw materials used and firing conditions.

For this reason, all the ceramic body were petrographically, chemically and mineralogically analysed by polarised light microscopy, X-ray fluorescence (XRF) and X-ray powder diffraction (XRPD), respectively, and the chemical data were statistically treated (principal component analysis and cluster analysis).

The chemical composition of this ceramic class resulted quite homogeneous, indicating the use of similar clay materials and preparation procedures, especially in terms of clay levigation. A low-calcium clay material, rich in both potassium and iron, was used. When samples are considered in diachronic terms, a progressive, although not drastic, change can be observed among them. Although the paste is quite fine, some medium and fine sand-sized inclusions indicates that the pottery was produced within the region and possibly in Barikot. As for its production technology, the mineralogical associations indicate that the firing temperature was in the thermal interval between 750°C and 950°C, and the presence of spinel and magnetite that the firing was in reducing conditions.

As for the slip, the microstructural analysis by scanning electron microscopy (SEM) indicates that it was obtained using a very fine-grained material, derived from the levigation of an iron-rich clay material. Moreover, the Moessbauer spectroscopy on the slip allowed to better constrain the production technology of this characteristic black polished coating.

# Shape and matter - Clay, terracottas and polychrome vascular paintings in Lipari (2<sup>nd</sup> half of the 4<sup>th</sup> cent. BC)

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Keywords: ceramic bodies, pigments, Lipari painter.

The comparison between objects of different classes as suggested by optical examinations, was deepened with experimental analyses (thin sections, SEM-EDX and XRF) revealed the presence of the same material components in the ceramic bodies and in the pigments of both the vessels and the figured coroplasty. A consolidated attitude in the past archaeological research, had led to divide the artisan expressions of Lipára in vases of the Lipari painter group and the pinakes or fictitious devotional tablets. Today, in light of a different reading of the chronologies, we can consider contemporary these two types of artifacts and attribute them to shops that used the same cooking methods. The evidence of the pigments (such as cinnaber) and the production methods leads to re-reading the pieces and reconsidering the analogies of the themes they propose. The female figures, who transfer into concrete and realistic attitudes in a superhuman world, reveal in spite of the differences linked to the support of formal solutions, schemes, symbolic objects and recurring chromatisms. Finally, the relationships with the formal experiences of Magna Graecia and Sicily reconstructed on an iconographic and formal basis do not seem to fully explain the revisits of the artisanschemes. At this point the certainty of links with other areas pushes to ask oneself if one shops of new ways, derived from the areas where the raw materials of the artifacts are imported, in an unexplored cultural climate that precedes the Hellenistic koinè.

Barone, G., Di Bella, M., Mazzoleni, P. Quartieri, S. Raneri, S. Sabatino, G. (2018): Pigments characterization of polychrome vases production at Lipára: New insights by noninvasive spectroscopic methods, X Ray Spectrometry, 47(1), 46-57, <u>https://doi.org/10.1002/xrs.2810</u>.

### Archaeometric characterization of Late Archaic ceramic from Erice (Sicily) aimed to provenance determination

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Keywords: painted geometric tableware, black-figures pottery, archaeometry.

A set of 20 ceramic samples was autoptically selected from the numerous findings recovered from the stratigraphic excavations of the late Archaic city walls of Erice (western Sicily), in order to be analysed with archaeometric techniques for provenance determination. The excavations were carried out between 2010 and 2014, as part of a research project funded by the Freie Universiät Berlin and the Fritz Thyssen Foundation. Specifically, the ceramic material consists of tableware with a painted geometric decoration of presumed local/ regional production, as well as apparently imported black-figures pottery. Both the categories can be traced back to a chronological period between the second half/last quarter of the 6th and the beginning of the 5th century BCE. The methodological approach was aimed to the characterization of the ceramic pastes in terms of relative abundance, size distribution and mineralogical composition of the aplastic inclusions by the observation of thin sections with the polarizing microscope. The objective of the microscopic observations consisted in verifying the existence of textural and/or mineralogical analogies to be ascribed to the same clayey raw material and, consequently, to the same production centre. The chemical analyses of the same set of ceramic samples were carried out using the ICP-OES and ICP-MS techniques (55 elements in total). The aim of chemical analyses was to verify the adequacy of the petrographic classification and identify any chemical marker useful for provenance determination. All the analysed samples of matt painted ceramic with geometric decoration have consistent compositional and textural characteristics, to the point of considering their assignment to a single "paste group". Specifically, it was found the use of very peculiar clay rich in calcareous bioclasts among the included aplastic and relatively poor in quartz and mica. The production, well distinguishable from those to date already attested in western Sicily, could be local. Concerning samples taken from the ceramic fragments decorated with black paint, the evidence derived from mineralogical-petrographic observations and chemical analyses help confirm their importation from extra-insular production centres, specifically from the Attic region. The Ca-poor paste and the peculiar concentration of many trace elements such as Cr, Ni, Co, As, Pb, Zn, Cu, Sc, Be, V, Ga, Ge, Sn, Tl in the ceramic body strongly support this hypothesis.

#### Raw materials for ancient ceramic productions from Campania region: provenance studies by means of Sr-Nd isotopes

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Keywords: Sr-Nd isotopes, archaeological pottery, provenance.

When archaeometric studies on archaeological ceramics are performed, one of the most important questions asked by archaeologists is the provenance of pottery. This is usually performed by comparing mineropetrographic and chemical composition of ceramics with that of local raw materials (clays, temper), production indicators and appropriate reference groups. Nevertheless, the commonly-used analytical techniques (e.g. OM, SEM-EDS, XRF, ICP-MS) may not always be helpful for the determination of provenance. Indeed, processing of raw materials, such as tempering or levigation, can significantly modify their original chemical composition, sometimes leading to an ineffective identification of raw material resources. For this reason, a pioneering analytical approach has been recently applied by measuring the Sr and Nd isotopic signature.

Isotope analysis has largely used in archaeological sciences to date objects and identify their provenance, making it also a useful tool for the determination of provenance of ceramic vessels (De Bonis et al., 2018 and references therein). For this study, <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd isotope ratios were measured on archaeological pottery from Campania and raw materials (clays and volcanic temper) exploited in antiquity for producing ceramics. The analyses were focused on samples from both the Bay of Naples and Southern Campania. The isotope signatures allowed us to better discriminate among different productions and find a strong relationship between the archaeological pottery and the geological sources of raw materials.

In order to validate the method, Sr-Nd isotope ratios were also measured for the first time on experimental ceramic materials that replicate archaeological pottery (De Bonis et al., 2018). It was interesting to note that synthetic mixtures used for the ceramic replicas plot exactly on the theoretical mixing curve between the clay and volcanic temper end-members. This suggests that the artificial manipulation of raw materials (firing, levigation, tempering) induces no significant variations to the Sr-Nd isotope fingerprint, which strictly depends on the geochemical affinity of the raw materials. Thus, isotopic analysis can be considered as an effective and robust method that could complement the common multi-analytical approach in order to more precisely constrain potential geological sources for ceramic materials and pottery provenance.

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#### Preliminary study of ovoid Baetican amphorae found in Gades (El Olivillo, Cádiz)

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Keywords: ovoid amphorae, organic residue analysis, Roman period.

The study of organic residues absorbed in kitchen and storage wares gives information about the vessels' use, the commodities stored or processed in the analyzed vessels, ancient trade, and the technological features of the ceramics such as their coating or potential repair (Evershed 2008). These studies allow to characterize the dietary habits of a specific period and, if interpreted in the framework of the context of use of the containers, of a particular social group. In particular, residue analysis can also be applied to amphorae in order to understand the content and therefore to go deepen in the study of ancient trade. Here we present the preliminary result of the analysis of so called Ovoid amphorae excavated in Cadiz during the El Olivillo project. The content of this typology of amphorae has not been studied until now, except for a preliminary test (Bernal et al, in press). The amphorae were sampled and analysed following the methods proposed by Mottram et al. (1999) for the identification of lipids, and Pecci et al. (2013) for the identification of wine residues. The preliminary results indicate that all the amphorae were coated with abundant resin or pitch from Pinaceae. Some of the amphorae show wine residues, but this is not the only content identified. The study is part of the project I+D RACAMed (HAR2017-84242-P) & Garvm II (HAR2016-78691-P) founded by the MINECO Spanish Ministery. It is also part of the activities of the ERAAUB, Consolidated Group (2017 SGR 1043) of the University of Barcelona, ICREA, the University of Cadiz, the contract RYC 2013-13369 founded by the MINECO Spanish Ministery.

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#### Blonde with blue eyes? The colours of Morgantina goddesses

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Keywords: cultural heritage, Morgantina, central Sicily.

The extraordinary spread of non-invasive and non-destructive methodologies to investigate cultural heritage has allowed scientists in recent years to focus on studying polycromy in ancient art. It is a very fascinating topic, not very well known yet but interesting to understand the original appearance of many archaeological findings that have lost their original colours. Studying pigments and painting techniques is today a matter of great interest not only for archaeologists and art historians but also for geologists, physicists, chemists, art conservators and restorers, making possible an effective cooperation among scholars specialized in many fields. The proposed paper aims to discuss the results of an ongoing multidisciplinary research project dedicated to polycromy in ancient Morgantina, a Sikel Greek settlement in central Sicily. Thanks to years of archaeological excavations conducted by an American archaeological mission here many findings (mainly terracotta statues and terracotta architectural ornamentation) with very well preserved original colours have been discovered. The research project, named "Morgantina a colori", starting in 2014 with the cooperation of the Regional Archaeological Museum in Aidone (Enna), has recently proceeded thanks to the valuable help of the European Research Infrastructure for Heritage Science (E-RIHS), in Italy funded by MIUR, and the cooperation of "Polo Museale di Piazza Armerina, Aidone ed Enna" together with "Centro Regionale per il Restauro". Carrying out non-invasive analyses (XRF, XRD, Raman spectroscopy) a large group of archaeological findings have been analysed with the aim of emphasizing the important role of polycromy in ancient Greek art between Archaism and Hellenism (Alberghina et al., 2014; Raffiotta, 2014; Raffiotta, 2017).

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#### Archaeometric and archaeological characterization of Medieval and post-Medieval tiles from S. Francesco's church, Savona (Italy)

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Keywords: ceramic tiles, archaeometry, provenance.

A set of ceramic materials - about 270 pieces, mainly consisting of bricks and tiles (terracotta and glazed ceramics) largely fragmented - was found during recent restorations under the flooring of a room overlooking the cloister of S. Francesco's church in Savona. The fragments were dispersed in the filling between an airspace structure of bricks and the current floor. These loose materials form an unusual archaeological layer, whose precise chronological and stratigraphic data are lacking. However, as the history of the monastic building and of the examined room is rather complex and poorly known, the ceramic materials were analysed in order to acquire information on the architectonic phases through material data.

At macroscopic scale the fragments showed typological and dimensional variability, thus were divided in groups with homogeneous characteristics. A representative sample of each group was analysed by optical microscopy (OM) and scanning electron microscopy (SEM) to obtain a full compositional and technological characterization. The analyses were aimed at identifying the provenance of the samples, and distinguishing different groups possibly to be related to different chronologies.

Petrographic analyses of the fabrics allowed identifying the local production, as suggested by the presence of: gneiss and amphibolite inclusions to be related to the local Palaeozoic basement, and calcareous (foraminifera) and siliceous (diatoms, radiolarians, sponge spiculae) microfossils associated with the Pliocene marine sediments outcropping in the area of Savona. The presence, on the majority of the pieces, of the so-called *graida* (grid) a feature typical of the tile production of Savona (*i.e.*, a sort of stamp on the back of the tile to ensure higher adhesion to the mortar), concurs with the geological markers in identifying as local provenance. The OM observations allowed inferring: firing temperatures of approximately between 800°- 900°C (partial decomposition of carbonates, partial vitrification of the clay matrix and dehydration of micas), and for the glazed tiles a good technical level (double firing, no residual inclusions or bubbles).

Unfortunately the lack of data for uncoated terracotta tiles in the area of Savona made it difficult to find temporal constraints, *e.g.*, through mensiochronological datasets. Only for some of the groups *ante* and *post quem* terms were established based on the correlation between the acquired dataset and bibliographical references. For example a group of green glazed square tiles has been dated to the end of XIII century, while a group of uncoated ceramics with a refined paste was dated to the XVI century based on archaeological evidences.

On the whole, the study allowed organizing the findings, characterizing the manufacturing process (provenance and firing techniques), and formulating hypothesis on the temporal evolution of the flooring of the room (*i.e.*, at least 3 different paving between XIII - XVI century).

#### The ancient pozzolanic mortars of the Thermal Complex of Baia (Campi Flegrei, Italy)

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Keywords: ancient Roman mortars, mineralogical and petrographic analysis, Campi Flegrei.

The excellent preservation state of mortars, artificial products deriving from geological materials, testifies the high technological level achieved by Roman construction workers. Builders knew that the combination of lime with special volcanic products (*pozzolana*), mortar and concrete become hydraulic, allowing underwater hardening and increasing mechanical strength. The use of pozzolana marked a revolutionary progress in construction, due to the ability of this peculiar mixture to cure underwater (hydraulic limes), with higher speed compared to carbonation processes of slaked lime. If volcanic materials were not available, fragments of bricks and ceramics, possessing same hydraulic properties of pozzolana, were used.

Aim of this research is the characterization of mortars from the thermal Complex of Baia, one of the most important archeological sites in the Campania region. The ancient *Baiae (Campi Flegrei)*, famed for thermal springs, was the holiday resort of the Roman aristocracy.

Thanks to the Superintendence of Archeological Heritage of Campania, we performed a non-invasive, but representative, sampling of mortars in order to reach our characterization scopes and provide useful information on probable future restoration activities.

Collected samples were studied by multiple methodologies (OM, XRPD, SEM-EDS, TGA, MIP). The results confirmed that Roman engineers extensively used tuff aggregate, hydrated lime, and ceramic fragments. In particular, the typical mineral association of phillipsite > chabazite > analcime points out the provenance of tuff aggregate from the Neapolitan Yellow Tuff (NYT) formation (de Gennaro et al., 2000), related to the *Campi Flegrei* volcanic activity, dating back to 15.000 years BP.

A relevant characteristic detected in all samples is the outstanding hydraulicity of these mortars, as shown by the reaction rims between pozzolanic materials and binder; this feature is supported by the Hydraulicity Index (HI) and thermal analyses investigations. Composition of the cementiceous binding matrix is particularly relevant, with the contemporary presence of gel-like C-A-S-H, derived from lime/ceramic fragments reaction, calcite and gypsum. The presence of calcite is likely connected to partial reaction of underburned lime. Finally, gypsum could be ascribed to sulphatation processes of calcite. These secondary minerogenetic products fill pore space and enhance bonding in pumice clasts, thus contributing to long-term durability of mortars. These results are also highlighted by porosity tests, indeed the main difference between ancient Roman mortars and modern hydraulic ones is the pore size.

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#### Accelerated ageing tests on carbonate stones and assessment of their recession rate

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Keywords: Stone recession rate, accelerated ageing tests, rainwater simulation.

Considering that recession rate estimates derived from available equations are not sufficiently reliable when applied to limestones, an experimental investigation was conducted to determine the possible correlations between stone recession of different types of carbonate rocks and petrographic and textural features by a series of aging tests under controlled environmental conditions.

In this study samples of carbonate stones differing in their textural features and mineral composition have been subjected to accelerated ageing tests in an environmental test chamber simulating the wetting effect of rainwater using two different water compositions corresponding to those of the Italian cities of Bologna ( $pH \sim 7$ , Panettiere et al. 2000) and Stresa ( $pH \sim 6$ , Rogora et al. 2004).

Bulk stone recession was evaluated considering sample weight loss as a function of the number of wetting cycles. Direct measurements of recession were performed by Confocal Microscopy (CM) which allowed 3D reconstruction of the stone surface and evaluation of differential recession as a function of textural features.

Measured recession resulted to be different with the two types of water used, clearly related to the variation in calcite solubility as a function of water pH. Recession resulted to be linearly correlated with calcite grain size, while porosity seems to have a minor effect. In addition, rock types containing significant amounts of clay minerals registered greater material loss.

Linear recession measurements allowed the definition of stone-specific phenomenological coefficients (N) to be applied to recession rate estimates obtained from the currently available recession equations for carbonate rocks (Honeyborne & Price 1977, Weber 1985). The effect of grain size on stone recession have been also discussed and quantified.

This work represents a pilot study in the identification of a rapid and efficient methodological approach able to determine the recession rate of a specific carbonate rock type in a given environment, in order to provide reliable estimates of future stone deterioration under specific environmental conditions from expected climate scenarios.

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### Petro-physical characterization of sandstones used in the buildings of the UNESCO World Heritage Historic Centre of Urbino (Marche, Italy)

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Keywords: sandstones, petrography, physical properties.

Many buildings of the Historic Centre of Urbino (Marche, Italy), inscribed on the UNESCO World Heritage List, are characterized by portals made of sedimentary rocks such as limestones and sandstones (Mazzini, 1982; Negroni, 2005). A local provenance from the nearby Apennines was already recognized for carbonate lithotypes (Mazzini, 1982; Amadori, 1985; Busdraghi & Wezel, 2002; Busdraghi & Veneri, 2003) whereas sandstones were never investigated. For this reason, very small sandstone flakes ( $\leq 1 \text{ cm}^3$ ) of already detached portions of damaged portals (not useful for any restorations) and samples from the best candidate quarry areas of provenance, were studied through thin section petrography. The investigation was addressed to the Sant'Ippolito area (30 km SE of Urbino) where a historical artistic stone craftsmanship and stonemason activity are well known (Savelli & Belacchi, 2000) and few clues of the ancient guarrying activity are still recognizable. The comparative petrographic study (through QFL classification diagram) on the fine- to medium-grained sandstones emphasized two different lithotype groups: (i) lithic arenites with predominance of bioclasts (both planktonic and benthic foraminifera) and (ii) feldspathic lithic arenites without bioclasts and richer in quartz. The whole data indicate that the investigated sandstones from the historic buildings of Urbino closely match with the so-called Sant'Ippolito Sandstones that represent an arenitic lithofacies of the Messinian p.p. Colombacci Formation (Tramontana et al, 2005; AA.VV., 2016). As a matter of fact, these lithotypes were used by the ancient stoneworkers of Sant'Ippolito since XIV century (Vernarecci, 1900). In order to gather useful data in planning possible restoration projects of the historic buildings, selected samples were also investigated to define their physic-mechanical behaviour.

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### Characterization of the building materials in the historic centre of Urbino (Marche, Italy): an alternative perspective for the fruition of the Cultural Heritage

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Keywords: Cultural Heritage, building materials, Urbino.

In the past, building materials used for the urban development of a city were the result of the availability of suitable geomaterials in the surrounding areas. Also the stones found in the historical buildings of Urbino, as well as the raw materials used for bricks and mortars, generally come from the local geologic formations (Capuano et al., 1989; AA.VV, 2009; 2010). Only in the case of some ornamental stones, used for monuments and decorations, and for which highly prized lithologies were chosen, an extra-regional or transnational provenance has been recognized.

This study is aimed to propose an alternative way for the cultural fruition of the UNESCO World Heritage historic centre of Urbino through the geo-lithologic characterization of the most used stones in buildings and walls. For this purpose, some monuments, palaces, portals (Busdraghi & Veneri, 2003; Santi et.al, 2018) and Renaissance Historical Walls (Busdraghi et al., 1992; 1994) with some other remains of Roman and Medieval age were considered.

A geo-lithologic information sheet containing the description and properties of the recognized building materials has been achieved for each investigated site. For obvious conservation reasons, no sampling were performed and only autoptic observations were carried out to identify different materials and the most probable provenance areas, together with detailed historical and bibliographic researches. The identification of ancient quarries allowed reconstructing the trade routes and cultural interactions, also giving useful clues in finding raw materials for recovery and restoration works.

Finally, for a better fruition of the Cultural Heritage of Urbino, the informative sheets of a "stones itinerary" of the building materials can be made available by means of Quick Response Code system (QR code).

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#### Mineralogy and pore space a key to salt weathering

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Keywords: salt weathering, porosity, durability.

Salt weathering is one of the most severe deterioration mechanisms, causing slow crumble to built heritage. Several studies have been carried out to assess the link between mineralogy, petrographic features (*e.g.*, texture, porosity) and Na<sub>2</sub>SO<sub>4</sub> salt weathering mechanisms. In this study the behaviour of three well-characterised carbonatic sedimentary lithotypes to different saline solutions was addressed. The selection of the different salts was designed to cover different possibilities of saline sources for built heritage, i.e. capillary rise, acid rains, atmospheric particulate deposition, bird or other animals scat, and de-icing salt contamination. The selected lithotypes: Breccia Aurora, Rosso Verona and Vicenza Stone, were tested through partial continuous immersion method to investigate their resistance to Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, NaCO<sub>3</sub>, NaCl, KNO<sub>3</sub> saturated solutions.

Both fresh and salt-weathered samples were analysed by means of petrophysical properties (*i.e.*, total immersion, capillary rise, hygroscopic absorption) and morphology (*i.e.*, Scanning Electron Microscopy (SEM)) to investigate the modification triggered in the porous network by salt crystallization. A complete mineralogical and morphologic characterization of the efflorescence crusts was attained through X-Ray Powder Diffraction (XRPD), SEM and  $\mu$ -Raman Spectroscopy. An appropriate description of the variation of petrophysical parameters such as density, mass, and porosity was carried out. These results were linked with the characteristics of the whole pore-network of the unaltered rock, to identify the main constraints influencing salt decay, and weathering susceptibility. The results highlight a higher decay rate for salts that can crystallize in different hydration stages at room temperature, and for bimodal pore distribution. The dataset offers a whole overview of the different salt induced weathering for the addressed sedimentary lithotypes.

#### Investigating a Byzantine technology: experimental replicas of Ca-phosphate opacified glass

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Keywords: Glass, opacification, Byzantine.

The present study focuses on a Byzantine opacification technique of mosaic glass tesserae, based on Ca-phosphate, and it is commonly accepted that animal bones were the source of this phase (e.g., Bonnerot et al., 2016; Neri et al., 2017). The micro-textural features of Byzantine tesserae with Ca-phosphate, independently from geographical location of mosaics, are quite homogenous, suggesting a well-established practise. The present work aims at clarifying the exact process of production in terms of firing temperatures and times, and eventual pre-treatments of bones, by means of experimental replicas. In particular, replicas were carried out in controlled melting conditions, which simulate those potentially applicable during Byzantine times, in order to obtain an opaque glass with micro-textures of glassy matrix, bone inclusions and reaction rims comparable to those identified in ancient glass tesserae (Silvestri et al., 2016). A single piece of bovine bone, to minimize the variables depending on species or individuals, mixed with silica-soda-lime glass, having chemical composition quite comparable to ancient natron glass, was selected. The bovine bone was used both as "un-treated" and after its preliminary firing at different temperatures (350, 450, 600 and 800°C), and was characterised by means of XRPD and ICP-OES. Two sets of experiments were carried out: the first one was produced by maintaining constant firing time (5 hours) and temperature (700°C), and cooling rate (quenching), and by using various bone samples (un-treated and fired at above different temperatures); the second one was conducted by using a single bone sample (that fired at 800°C) and by varying firing times (18 and 36 hours) and temperatures (700 and 1100°C), and cooling rates (quenching and slow cooling). The replicas were all characterised by means of SEM-EDS and micro-Raman spectroscopy. Results demonstrate that the production of Caphosphate opacified glass requires a preliminary firing of bone, a temperature of about 700°C and long firing times (up to 36 hours). The use of unfired bone did not give satisfying results, as well as short firing times (5 hours), because the micro-textures obtained are not similar to those identified in ancient samples. The use of higher firing temperatures (1100°C) can be also excluded, independently from firing times, as it produced a transparent glass.

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### Marble Decoration of the Roman Theatre of Urbino (IT): A Multi-Method Provenance Approach

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Keywords: marble provenance, archaeometry, roman italy.

Roman society was highly hierarchical and the elite were constantly striving to showcase, maintain and increase their power and prestige. Gifting buildings and donations of individual architectural elements such as marble decoration, columns or statuary were amongst the most powerful means of achieving this (Zuiderhoek, 2009). One of the most favoured buildings for elite munificence was the theatre. Within the Roman theatre, the orchestra and the *scaenae frons*, the lavishly marble decorated background of the theatre stage, was specifically important as a medium of propaganda.

This paper presents the results of the provenance study of the white and coloured marbles used for decorating the Roman theatre of *Urvinum Mataurense* (modern Urbino, Marche, Italy). The provenance of the white and greco scritto-like marbles was determined using a minero-petrographic approach in combination with X-ray diffraction and stable isotopic analyses of carbon and oxygen. Coloured marbles were identified macroscopically based on the experience of the authors and by comparison with reference samples and available image databases.

The Roman theatre of Urbino was constructed in the late 1st century BCE or first half of the 1st century CE (Luni, 1977). In the 2nd century CE, the building was renovated and its marble decoration was installed (Delpino & Valli, in press; Luni, 1977). Marble was used for floor and wall revetment of the orchestra and scene building, and for the columnar architecture of the scene building which was decorated with monolithic columns in coloured marble.

The analytical data show the presence of Carrara (Italy) and Proconnesos (*Asia Minor*) white marbles, and greco scritto from Hasançavuslar, Turkey. A multi-coloured effect was created by combining coloured marbles from the Italian Peninsula, Greece (mainland and Aegean islands), North Africa, *Asia Minor*, and to a lesser extent the Eastern Desert in Egypt. The marble panorama shows that the town, like the entire region of central Adriatic Italy, was well integrated in the wider Roman marble trade network. In comparison to contemporaneous theatres, the Urbino theatre is particularly remarkable for the sumptuousness of the marble renovation, especially in terms of the number of marble varieties applied, which shows the opulence of the town and its local elite in the 2nd century CE.

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#### The Bricks of Hagia Sophia: compositional study and archaeometric consideration

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Keywords: Bricks, Archaeometry, Hagia Sophia.

This works describes the compositional study of 29 brick fragments coming from different areas of Hagia Sophia museum. It is part of an international collaboration between the University of Mexico, Hagia Sophia Museum in Istanbul and the Department of Biology, Ecology and Earth Sciences of the University of Calabria (Barba et al., 2016; Cappa et al., 2015; Cura et al., 2014; Miriello et al., 2016).

The aim of this work is to obtain a geochemical and minero-petrographic characterization of the samples, through the application of different diagnostics techniques, and to build an interactive 3D GIS to manage the obtained data.

The brick fragments of Hagia Sophia were studied by Polarized light microscopy (OM), X-Ray Powder Diffraction (XRPD), X-ray Fluorescence (XRF), Thermogravimetric Analysis (TGA) and Energy Dispersive X-ray Spectrometry (EDS) by Electron Probe Micro Analysis (EPMA). In addition, the geochemical data obtained were processed through cluster analysis, in order to highlight compositional similarities and differences among the samples and to verify if the clusters of bricks identified are linked to the different constructive phases of the building (Mainstone, 1988). Furthermore, the study allowed us to obtain information about the raw materials employed and the production technology of the bricks.

The data collected through the application of the various diagnostic methodologies have been loaded in GIS environment in order to create the first GIS based cartography of the monument. Data could be interpolated in 3D dimension to obtain new derived layer based on the spatial distribution of geochemical and mineropetrographic data.

This system can be used to support diagnostic analysis for the cultural heritage and to help the technical staff of the Hagia Sophia Museum for planning future restoration works.

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## Glass in imitation of exotic marbles. An analytical investigation of Roman *opus sectile* tessera from Gorga collection

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Keywords: Roman glass, ancient marbles, glass technology.

The materials uncovered in excavations in several provinces of the Roman empire provide important evidence to the extensive use of glass in the most precious *opera sectilia*. These are mostly sporadic discoveries consisting of few items whose dating is often difficult.

For this reason, the about 26.000 monochrome and polychrome glass pieces imitating marbles, rare stones or with fanciful patterns from the collection belonged to Evangelista Gorga (1865-1957), are a mine of valuable information on the Roman glassmaking technology, especially on coloration and working techniques (Saguì et al. 2012). The secrets of the yellow colouring techniques were recently investigated (Verità et al., 2013) and specific investigation on red colouring techniques are in progress at the VICARTE (Universidade Nova de Lisboa) in Lisbon.

The homogeneity of this unique collection points to a single context as a source. The archaeological studies performed on these glass fragments attest their probable provenance from illegal excavation occurred in the 19<sup>th</sup> c in the villa of emperor Lucius Verus (161-169 AD), an adoptive brother of Marcus Aurelius, located on the via Cassia, Rome (Bacchelli et al. 1995).

A recent collaborative study involved the archaeologist who discovered, studied, classified and illustrated the glasses of the Gorga collection and the experts on ancient stones and glass of the LAMA laboratory of Iuav University of Venice. The aim of this research is to investigate the opus sectile pieces made in imitation of real stones. Glass pieces imitating a dozen of antique marbles and exotic stones have been identified.

Samples were selected for analysis. Quantitative chemical composition was determined allowing the types of glass used and the colouring techniques to be identified. Results are compared with similar data obtained by studies on coloured Roman glass and mosaic tesserae. Similarities and discrepancies are discussed and hypotheses are suggested on the technology and provenance of this extraordinary Roman production.

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# Proposal for the study of ceramic production in the Argar. The case of the settlement of Peñalosa (Baños de la Encina, Jaén)

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Keywords: Pottery, technology, archaeometry.

In this work we show a methodological proposal for the analysis of the manufacturing technology of the vessels found in the Argaric settlement of Peñalosa (Baños de la Encina, Jaén), a reference point in the study of this culture, due to the good conservation of its structures and the archaeological material found in this site (Cortés et al., 2000). The limited technological information that we can obtain through a simple visual examination of the ceramics, creates the need to use alternative methods for their analysis. The methodology proposed here is based on the application of analytical techniques from Earth Sciences (stereomicroscope, X-ray diffraction, Raman Spectroscopy, petropraphy in thin section and X-ray fluorescence) that have as their main objective the characterization of surfaces and ceramic pastes. The aim of this study is to respond to certain aspects of the sequence of ceramic production, the degree of standardization of the same one, as well as the origin of the raw material of vessels. Likewise, the existence of well-defined contexts in the village under study, facilitates the possible distinction between those productions found in domestics contexts, such as those documented in funerary contexts. Finally, through the application of previous analytical techniques in ceramic containers, we will be able to obtain information of a social, economic and ritual nature in the Argar culture.

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#### Mineralogical study of a pair of Bronze Age plaques from the Erlitou culture, China

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Keywords: Chinese Bronze Age, Erlitou culture, Henan Province.

A pair of plaques from a private collection showing stylized faces, probably representing mythological animals originating from the Chinese Bronze Age Erlitou culture (2000 - 1500 BC), Henan Province, China, were studied. They consist of bronze plates (14.1 x 9.5 and 13.8 x 9 cm) with white, light blue to darker blue inlay material. A small number of similar plaques from this culture are known and they were made by inlaying prepared pieces of turquoise into open cells to form the animal mask. Characteristic elements of all these masks are the symmetry, the raised eyes, small eyelets which would be used to attach to clothing and the use of mostly rectangular inlay.

The shape, size, style and the bronze frame of the two studied masks correspond to the known plaques from the Erlitou culture however, the material used as inlay is different. Microscopic investigation revealed that two different materials were used. By microspot X-ray diffraction experiments (Malvern Panalytical Empyrean Diffractometer, Cu radiation), both types were identified as calcite, sometimes with traces of quartz. No other crystalline phases were detected. The material used as the main inlay component is white to light or darker blue, sometimes also greenish to greenish-blue, often not homogeneously coloured and occasionally cut by thin, black veins. The inlay is of irregular shape, mostly elongated (up to 5 x 1 cm in size) and corresponds to a natural rock (limestone or marble). The second material has a light to darker blue colour and is composed of very small, white crystals (< 0.05 mm) in a fine-grained matrix. Common are small, round cavities (max. 0.5 mm in diameter) like air bubbles. Additionally, a small fragment of wood fibre was detected. This material was artificially prepared by grinding limestone or marble to a powder, and then a binder, so far unidentified, was added to create a paste.

The plaques were created by fixing an openwork bronze frame outlining the contours of the face of the animal to a solid bronze plate resulting in open cells at the front. These cells were filled with the calcite-containing paste. The prepared strips of limestone/marble were then pressed into the cells. After drying, the surface was sanded and polished and finally the raise, globular eyes were glued into place. The use of calcite could indicate that the studied pair pre-dates the turquoise plaques, also a paste made of calcite was not observed in the other plaques.

Microspot X-ray diffraction showed that the bronze had undergone intense corrosion. The most common alteration product is rouaite,  $Cu_2(NO_3)(OH)_3$ . Additionally cuprite, malachite, anglesite (the bronze is rich in lead), nantokite and romarchite along with possibly niter and  $Cu_2(CO_3)(OH)_2$ ·H<sub>2</sub>O were identified. As the original color of the calcite was white, the discoloration to green/blue is a result of copper migration from the bronze over time. To our knowledge, this is the first time rouaite has been identified as a corrosion product of an antique bronze, indicating that the plaques stayed in an environment rich in nitrate.

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### **Session S31**

### Mining sites: from industrial heritage to cultural heritage

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### The Abandoned Great Montevecchio Mine: From Industrial Heritage to Cultural Heritage

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Keywords: Sardinia, Montevecchio mine, industrial heritage.

The Great Montevecchio mine is located a few miles NW of Arbus and Guspini villages in SW Sardinia. The great Montevecchio mine exploited the richer and very large peripheral mineralized bundle of whole area, that is known for approximately 10 km in length and 600 m in depth, with maximum thicknesses for the individual veins from 1.5 to 7-8 m.

The useful mineralization include galena, sphalerite and cerussite, with subordinate acanthite, pyrite, chalcopyrite and arsenopyrite, in gangue of quartz, ankerite and siderite, and more rare calcite and baryte. Secondary minerals are cerussite, anglesite, pyromorphite, smithsonite and brochantite. In particular, the emerald green in colour anglesite is the mine's hallmark mineral.

In 143 years of industrial activity the Great Montevecchio mine developed in five mining concessions referred as Genna Sciria, Piccalinna, Montevecchio I, Montevecchio II, Montevecchio III. According to their geographical position respect to the homonymous village, built to the development of the mining life, an eastern and western zone is distinguished, where the mineralized bundle tooks the names of S. Antonio, Piccalinna, Sanna, Telle and Casargiu derived from the mines that were prepared for the ore deposits exploitation.

In addition to industrial production, mining has been also experimentation and technological research of high level. The wise management and the technical and scientific experience of managers and technicians has allowed the creation of structures, systems and machines that have revolutionized the mining operation by improving productivity and safety of the workplace. Montevecchio was culture and technology, and exported worldwide mining technology.

The whole Arburese lode system is of worldwide size, one of the most impressive in Europe.

Together with the other neighboring Ingurtosu and Gennamari mines Montevecchio boasted the richest concentration of lead and zinc minerals in Sardinia, having produced over 1,700,000 t of lead metal and about 1,200,000 t of zinc metal as well as silver, bismuth, antimony, copper, cadmium and germanium.

Five museums can be visited: The "Alberto and Giovanni Antonio Castoldi's Collection", which represents part of the family treasure. The museum of minerals, consisting of a rich collection from Montevecchio's minerals and other mines from Sardinia and Italy. The Museum of Dioramas dedicated to the history of mines from antiquity to the present day.

The building of the management that was the seat of the offices, the archive, the residence of the director and servants' quarters. In particular, the large meeting room is also known as the "Blue Room" for official meetings and receptions, where all the period furnishings have been expertly rebuilt. Through an underground route it is possible to visit the "Galleria Anglosarda", excavated starting from 1852 in order to mine the S. Antonio ore body.

### The National Solid Georesources database (GEMMA) at the Geological Survey of Italy

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Keywords: Mine, Geodatabase, Georesource.

The current state of the activities for, and knowledge about, the extraction of solid minerals in Italy is strongly heterogeneous. One main reason was certainly the transfer of the ruling and supervising competences from national to regional and local authorities. Indeed, the present institutional and regulatory system makes it extremely difficult, at the national scale, to reconstruct a clear picture of the Italian georesources and represent the current environmental status of extraction sites.

In this framework, the Geological Survey of Italy (SGI) of ISPRA is developing a geodatabase aiming at collecting all relevant information from available sources (CARG project, national census of active mines and quarries, data reported in the regional/provincial extraction plans, inventory of historical mining sites, network of national parks and mine museums, etc.). Taking advantage of the preliminary results of the Minerals4EU project (Minerals Intelligence Network for Europe), the PostgreSQL database is being designed with an INSPIRE compliant architecture.

The main purpose is to define the national situation of solid mineral resources including the geological, environmental and economic aspects, with particular attention to the environmental impact of mining practices and the potential exploitation of the decommissioned mining assets and the extracted waste piled up over time.

So far, all the active quarries and mines within the national territory have been identified and geo-referenced. About 90% of the mines opened since 1870 have been located too.

Each coded mining site has associated information related to data sources, type of mining site, state of activities, type of extracted ore, type of management, environmental situation of the site. The estimate of the resources and reserves amount is more problematic.

Due to the partition of competences attributed to the regional authorities by the Italian legislation, it is necessary to establish contacts and make agreements with a fairly large number of local bodies, each one with different rules and capabilities that must be considered and respected. Therefore, for the success of this project it is essential to build flexible spaces of dialogue and loyal collaboration. Within these areas of dialogue, the Geological Survey of Italy hopes that GEMMA can become a valid support tool for the development of national and regional policies oriented towards the sustainable production and efficient use of primary and secondary mineral resources, in a circular economy perspective.

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Keywords: lignite mines popularization, new technologies, Stilo-Capo d'Orlando Formation.

Agnana Calabra and the surrounding area is well known since the nineteenth-century for the lignite mines and its interesting geological and stratigraphic context. Fossils attributed to *Anthracotherium magnum* Cuvier comes from the lignites, and represent an important datum in the Italian fossil record. Moreover, particular ichnofossils are concentrated in lignite levels, which have never been recorded in similar geological and mining contexts all over Europe.

Lignite layers belong to the Stilo - Capo d'Orlando Formation (Oligocene-Miocene), constituted - from the bottom to the top - by conglomerates, lignites, sandstones, pelites and marls, which represent a transition from continental to marine deposits.

During the Bourbon regency ("Regno delle due Sicilie"), some mines of lignite was exploited in Agnana, for the use of coal by local populations as well as for export to the coastal towns near Agnana. After the unification of Italy, the Agnana mines ceased their activity around 1910 due to lack of funds.

Nowadays there are four main mines preserved in Agnana area: one is almost entirely safe to visit; two others preserve the entrances, but have not been recently explored and their safety has not been tested. The last and larger one has been exploited in the nineteenth century. Although walled up, its monumental portal is preserved with the dedication "Galleria Principe di Napoli".

The Agnana area has been classified as a SIC site of the Reggio Calabria province.

Recently, the Municipal Administration, with the collaboration of a researcher's team, is trying to establish the Mines GeoPark for cultural and touristic purposes, and started works to trace paths with wooden fences and picnic areas. Moreover, the other mining tunnels will be secured in a short time.

An Android/Ios application available for smartphones and tablets is planned, in order to provide an innovative online database on mines and on the geological-stratigraphic-paleontological-ichnological context of Agnana. This "AgnanaGeoDocuApp" will be accompanied by textual information, photographs, geological audiovisual documentaries addressed to visitors, tourists, trekkers, researchers, students and local people.

Furthermore, an original comic book is planned to expose and popularize the geology and paleontology to children. This "HippoPig" comic speak about the *Anthracotherium* life in the Oligocene Agnana paleoenvironment.

The mining site of Agnana represents a Regional Cultural Archaeo-industrial Heritage. A deeper knowledge and enhancement of the territory focused on its naturalistic, geological, paleontological and ichnological evidences can contribute to a better touristic attraction.

### Streppenosa mine: from geological singularity to geotourism opportunity

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Keywords: Hyblean plateau, Asphalt, Disused mine.

Art.136 of the Italian Code of Cultural Heritage and Landscape recalls the concept of "geological singularity" already expressed in the old "Regulations for application of landscape law 1497 of 1939".

The Streppenosa Mine, one of the many disused in the asphalt mining area around Ragusa, has all the characteristics to be considered such; it encapsulates a mixture of industrial archeology and geomorphological processes.

Exploitation of "pietra pece", from which road asphalt was extracted, has only two sites in Italy: Ragusa in Sicily and the mines of the Majella in the province of Pescara (two parallel stories in terms of events, processing techniques and geomorphological processes).

The geological singularity of the abandoned mine is enriched by history and stories; in fact, even before being used as a road finishing product, "pitchstone", was known in architecture both as a decorative ornamental stone, given its good sculptural workability, and for its characteristics of impermeability and therefore used against rising damp.

The geographic location of the mine, at the centre of the UNESCO triangle of Hyblaean Baroque (Ragusa, Modica, Scicli), makes a visit to it an exploration into the history of the monuments built after the catastrophic earthquake of 1693 which razed most of the pre-existing Renaissance buildings to the ground.

Located in the lower valley of the river Irminio, the main watercourse in the territory of Ragusa, this mine is a natural beauty inserted among unique landscapes associated with limestone outcrops of the Ragusa Formation and the dense network of dry stone walls born of the stone clearance of lands started in the Middle Ages to divide properties and create terraces for cultivation in steep areas.

In 2002, the Sicily Region acquired 120 hectares of land containing, in addition to the Streppenosa Mine, other underground and open-cast mines, and mining buildings and relics with historic value. Today, going down into the Streppenosa Mine - abandoned by the German Kopp brothers company in 1914 at the beginning of the First World War and never activated due to the lack of interest shown by the advent of oil exporation - the visitor still seems to be walking among the miners; the stone is stacked, ready to be taken away, the tracks and some wagons in the flooded area give an understanding of the fatigue of these men in bringing to the surface the stone that would then be loaded by the Pozzallo loader to asphalt the roads of Germany.

For more than a century nature has spread karstic features in the disused mine that make it unique compared with others in the area: stalactites steeped in oil, columns and calcite flows, conches and hints of stalagmites, but also an area rich in pisolites formed through the action of water and wind.

These are the ingredients of a visit to the abandoned mine: history, nature, fantastic landscapes to photograph, but also taste paths and a pristine sea not far away.

Thus, from geological singularity to geotourism opportunity, demonstrated by the substantial flows of visitors and scholars that the "Museo Regionale dell'Asfalto di Castelluccio e Tabuna" (established under Art. 2 of Regional Law 17 of 1991) has recorded in recent years, even though it has not yet been officially included in regional tourist circuits.

# Archeological Mines Park of San Silvestro (Tuscany) - Protection, valorisation and management of a mining landscape, practices and future plans

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Keywords: Archeology, mining landscape, heritage.

The Archeological Mines Park of San Silvestro is part of the larger system of the Val di Cornia Parks. The project of the open-air archeological and mining museum derived from a specific research background, that started with the archeological excavation of the medioeval castle of Rocca San Silvestro. The area is reach of traces connected to the exploitation of metalliferous resources, started at the end of the bronze age and ended in 1979, when the last mine closed (Semplici, 2011).

The aim of the Park, opened in 1996, is to protect and give value to the historical landscape, the result of centuries of mining activity. The management was entrusted to a in public company, the Parchi Val di Cornia spa, whose shareholders are the five municipality of the area. In twenty years, thanks to public funding, the impressive ruins of the medieval village of San Silvestro and two of the modern mining tunnels, have been restored and equipped for guided tours. Some of the buildings, originally used for productive and administrative purposes, house museums, services for visitors and information center (Guideri, 2008). Parchi Val di Cornia spa is working in order to compensate for losses on the cultural services and maintaining the environment, through business and marketing activities within the parks. The existence of a "cultural enterprise" in the Val di Cornia area is thus enabling very important results to be achieved, results which would otherwise be unobtainable. However much still remains to be done, for example improve the accessibility of ancient mining works and for this reason we are working on the accessibility of ancient diggings and in the equipment of some of them for the visit, real or virtual (Brocchini et al., 2017).

Increasing heritage awareness is still a key in the planning of future developments that bring both economic and cultural returns (Borgognoni & Guideri, 2008). The action of the ReMi network is necessary to connect sites which manage and enhance Italy's mining heritage and aims to set up a technical group to put forward suitable, consistent and agreed solutions to the problems listed above, and to enhance the specificities of the various mining areas.

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# The mining area of Comitini (near to Agrigento) and the "Solfara Sale" system: contribution to knowledge for the tourist-cultural recovery of a disused mining site

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Keywords: disused mining sites, industrial archaeology, mining parks.

Within the mining area of the district of Comitini in the province of Agrigento (Sicily), containing a lot of structures dating back to the period of sulfur exploitation on the island, there is the mining system of the "Solfara Sale" (Solfara in italian is a sulfen mine and Sale is the name). The mining complex, is made up of a system of tunnels and descents. Some parts of the underground structures, today appear in a good state of conservation and it can become potential sites for a tourist conversion as examples of industrial archeology. As part of the study carried out, the interest was concentrated on the mining structures considered most relevant, performing on them technical insights aimed at verifying the conditions of the hypogeal environments, both in terms of structural safety of the tunnels and environmental conditions (temperature, humidity, possible presence of gas, etc.), with the aim of being able to verify their potential usability. To this end, the plano-altimetric survey of the "Solfara Sale" tunnel and of n. 2 discendes of the system with the relative three-dimensional restitution were carried out, and the conditions of the global structural stability were verified. Finally, the environmental measurements within underground (presence of gas, temperature, humidity, air flows, etc.) were also carried out. The overall results of the investigations carried out were subsequently elaborated indicating the existence of the conditions for the possible tourist conversion of the site.

# An educational path inside a mine to rediscover the history, the tools and the techniques for mining fluorite in the Prestavèl mine (Trento Province, Italy)

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Keywords: Stava Valley, 1985 disaster, Prestavel tailing dam.

The Stava 1985 Foundation (a Registered Charity) is committed to keeping alive the "active memory" of the Stava Valley catastrophe, which was one of the worst mining disasters in the world. On 19<sup>th</sup> July 1985, 268 men, women and children were killed by a huge mudflow caused by the collapse of two tailings dams storing the waste of the fluorite enrichment process at the Prestavèl mine plant. The memory of this tragic event aims to avoid such disasters happening again, so that these innocent victims did not die in vain.

The goal of "active memory" is to improve the culture of safety, respect for the environment and correct and sustainable use of natural resources, which was lacking in Stava. Only this new awareness and sense of personal accountability can avoid the repetition of similar, foreseeable and avoidable disasters. In order to maintain this active memory, proper information must be provided on the origin and causes of the Stava Valley disaster and the responsibilities involved.

The Stava 1985 Foundation has made available a great deal of information and carried out several educational projects. Information about this disaster is based on the results of the criminal trial, which led to the conviction of 10 defendants, guilty of the crimes of negligent disaster and multiple manslaughter, and on the scientific investigations carried out after the incident.

Although it is possible to provide detailed information on the working of the mineral and the planning, growth and failure of the tailings dams, information on the history of the Prestavel mine and the mining activities is much more fragmentary.

Together with the Trento Autonomous Province, the Territorial Community of the Fiemme Valley and the Municipalities of Tesero, Cavalese and Varena, where the Prestavèl mine is located, the Stava 1985 Foundation aims to investigate in depth the history, tools and mining techniques at the Prestavèl mine. Access to this knowledge will be made more available thanks to the implementation of a short educational path in the initial stretch of the mine tunnel, at an elevation of 1550 m a.s.l., and an itinerary inside the tunnel, at the elevation of 1787 m a.s.l., with access on both slopes of Mt. Prestavèl. The works planned to make these two tunnels safe and accessible to the public are not particularly difficult or expensive.

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# The new value drivers to enhance abandoned mining sites: empirical evidence from the highest mining site in Italy

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Keywords: Mining site, business opportunities, touristic development.

During the last centuries the Italian mining sector gave a substantial contribution to the economy of the country representing one of the key points of the Italian Industry that has got a long and glorious tradition.

After the Second World War, the sector experienced a general decline that in parallel to the discovery of new markets and to the globalization of new materials has brought to the closing of many mines that were in the past among the main sources of our country.

Today, the exploitation of disused mining sites represents a relevant issue: the abandonment of these large places represents a significant element of degradation within the territory. A significant strategy to enhance these abandoned sites is given by tourism. Mining sites are rich of history and traditions and their architectural conformation makes these places characteristic and very suggestive.

The aim of the paper is to highlight what are the best business opportunities to transform an abandoned mining sites with a special focus on a touristic development through an emblematic case study located in Cogne (Italy). Using a comparison approach between different kind of exploitation solutions, is possible to find advantages and disadvantages of each ones.

The former mine was exploited for more than 5 centuries for the extraction of magnetite for iron production and it was in Italy one of the main mines of its type. From 1978 to 2016 the mine was closed and then, thanks to a new project of tourist development, it has started its second life as a tourist attraction.

The results of this research highlighted the great potential of these abandoned places. Through the business model developed for the Cogne mine it was possible to highlight the major problems in terms of design of these sites, economic, policy and social ones that characterize such interventions.

The business model implemented for the case study is based on an historical, cultural, natural and geological approach strongly focused to the area where the mine is situated, preserving and improving its history. The local community has a central role in this process of strong renovation through its political figures and through the ideas of the population represented by a cooperative society that manages the mine site. Finally, costs related to this transformation are relevant. For this reason, it is important to plan business strategies able to involve many stakeholders.

### Projects for the "Mine-museum " in the Cozzo-Disi dismissed site

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#### Keywords: cultural heritage, mining activity, Sicily.

Facilities, architectures and landscapes of abandoned mining sites constitute a huge cultural heritage. It began to become aware that the places of mining work could become places of culture, that structures and mining facilities could represent assets and that mining history constituted a collective experience not to be forgotten, rather to be capitalized in the construction of a stronger one social identity. The program launched by the Sicilian Region with Law 17/91 identified the main solfiferous sites no longer productive as places to be musealized. Until now, however, we have seen an enhancement action aimed more at protection and conservation, less at the fruition.

Behind the heterogeneity of the experiences, it is possible to discern a common base of intent: an enhancement project that addresses all the components of the cultural heritage (mining, archaeological-industrial, historicalurban, landscaping, environmental, archival, ethno-anthropological, etc.); the extension of protection from individual sites to the whole landscape that includes them; the reading of the mining territory in terms of extended "cultural landscape" interested by the mining activity; the search for roots in the territory that reinforce the development of a local identity.

All the Sicilian experiences have a common denominator that is the model of the "open-air museum": instead of proposing a collection inside a container, a collection of buildings and artefacts outside, in their original location, is exhibited. This model is certainly valid for the Cozzo-Disi mining site, the only Sicilian "mine-museum", where it is still possible to access real cultivation galleries, which would complete the surface itineraries in sequence to the places corresponding to the different phases of mineral treatment, in a spatial continuum.

The experimentation of this museum model has been deal with for some time in the Department of Architecture at the University of Palermo, projects developming for the only Sicilian mining site, where all the expressions of the extraction and production of the mineral, succeeded in the Sicilian sulphurous industry, are still present, from the beginning of the 19th century with the various forms of "fusion" to end with "floatation" in the 80s.

The proposed contribution shows the results of these projects as a verification of the museum management model expected for the "mine-museum", in relation to the museum space extended to the whole site, also in the subsoil, and to the territorial context concerned, with redefinition in cultural terms of the whole "mining landscape", now distorted because of abandonment and neglect. The proposed projects can serve to define the guidelines for the necessary architectural interventions, set-up and restoration, aimed therefore at the musealization of other solfiferous sites.

### The mining sites of historical or ethno-anthropological interest: a proposal for their cataloguing

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Keywords: Mining sites, historical interest, ethno-anthropological interest.

Despite the great Italian mining tradition - which in the past produced some of the largest mining operations in Europe - and although three thousand mining centres active in the period 1870 - 2006 (Berry et al. 2011) have been identified so far, mining sites have often been perceived as a legacy to be forgotten, also in relation to the significant environmental problems that mining has often caused in the territories concerned.

In recent years, however, there has been a reversal in the trend and the mining sites of historical or ethnoanthropological interest have started to be seen as an extraordinary opportunity, also in the light of the processes started on a European scale and thanks to the Code of Cultural Heritage and Landscape that recognized them as real cultural heritage. Furthermore, thanks to the important work carried out by the Italian mining parks and following the creation - in 2015, by ISPRA - of the National Network of Italian Parks and Mining Museums (ReMi), a virtuous path has now been set in motion for the valorization and musealization of these important realities. It is evident that from this process derives a series of procedural fulfillment, including cataloguing that can be defined as the systematic organization of knowledge relating to a cultural asset and typically consists of the classification, registration and description of the asset itself.

It is therefore clear that the cataloguing can play a decisive role in the process of protection, conservation and enhancement of these mining sites which often also acquire a wider cultural interest, being characterized by a system of values in which elements of architectural, scientific, naturalistic, environmental, landscape, technological, industrial and economic significance can be found. Since the recognition of the presence of useful minerals and the first attempts at exploitation often go back several centuries or millennia before our era, mining sites can also have an important archaeological significance.

Since there is no type of data sheet dedicated to mining sites of cultural interest among the many cataloguing standards defined by the Central Institute for Catalogue and Documentation (ICCD), a proposal related to the definition and adoption of a specific cataloguing standard for such cultural heritage has been drawn up.

Berry, P., Bandini A., & Dacquinoe, C. (2011): Classificazione dei siti minerari sotterranei abbandonati mediante un indice di rischio statico-strutturale, in Agata Patanè, a cura di, Recupero e valorizzazione delle miniere dismesse: lo stato dell'arte in Italia, atti del convegno (Rimini 9-11 settembre 2009) Geoitalia 2009 - VII Forum Italiano di Scienze della Terra - Sessione V3, ISPRA, Quaderni - Ambiente e società n. 3/2011, pp. 31-44.

# From mining to cultural and touristic resource of the territory. Examples of the Monte Arci area in the geological mining historical and environmental Sardinia Unesco global geopark

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Keywords: Sardinia, Masullas, obsidian.

In its mission to enhance and promote the knowledge of the abandoned mining areas of Sardinia, the Geological, Mining, Historical and Environmental Park of Sardinia started various activities for the enhancement of geosites which in a remote and recent past have been the subject of mining activities

In particular, in this work two representative geosites are described, located in the territory of Monte Arci in Marmilla (Oristano, central-western Sardinia) characterized by a particularly significant scientific, educational and cultural potential.

The first geosite is represented by the Obsidian Park of *Conca 'e Cannas*, opened to the public on 23 October, 2016.

This site, located along the southern slope of the impressive volcanic relief of Monte Arci, assumes considerable importance as it hosts the largest and most quality of the whole Mediterranean obsidian deposit.

Obsidian has been intensively exploited by prehistoric man since the beginning of the Neolithic, over 8000 years ago for the production of everyday objects such as knife scrapers and arrowheads.

Due to the particular obsidian attitude, which forms nuclei inside the rhyolites in perlite facies, the *Conca* 'e *Cannas* deposit since the 50s of the last century has been the subject of industrial mining for the perlite, undergoing volumetric changes and altering the initial state of the places.

The recent enhancement interventions by the municipality of the authentic village of Masullas and in conjunction with the Geological, Mining, Historical and Environmental Park of Sardinia have given back to the public an important historical-naturalistic site, reinforcing and making the link between culture and the environment particularly evident.

The other geosite examined is the abandoned mining site of *Nuraghe Onigu*, which for some time exploited a very special Miocene fluorite mineralization of Miocene age during the fifties of the last century, which certainly represents a *unicum* in the Sardinian mining and geological panorama, considering that all the most important fluorite mineralizations in Sardinia are typically Paleozoic.

The recovery and making safe will ensure full use of the site, which at the top of the hill stands the *Nuraghe Onigu*, archaeological monument considered the best preserved of all the local territory.

The recovery of this site will be added to the geotourist and cultural offer today proposed by the authentic village of Masullas together with the Natural monument of *Su Carongiu de Fanari*, known as "megapillow" and the already mentioned obsidian deposit of *Conca 'e Cannas*.

The GeoMuseo Monte Arci "Stefano Incani", which has been operating since 2010, acts as a glue for the transmission to the public of the rich geodiversity of the Marmilla territory and the whole Monte Arci.

# An alternative kind of re-vegetation. Feasibility of environmental restoration on a depleted mining site

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Keywords: Quarry, reclamation, recovery plan.

Quarries represent important economic activities with an high cost in term of environmental impact. Here we present a study of a quarrying site in Tuscany (Italy). The extracted lithotype, formerly "Arenaria di Manciano" consisting of medium-coarse arenites with intercalations of conglomerates. Some of the quarry-exposures of the Manciano Sandstone allow a detailed analysis of sedimentary structures, icnhofacies, fossils, etc., deserve to be preserved and emphasized. However other less interesting areas of the quarry, from the scientific point of view, need an environmental restoration at the end of the mining activity. Almost every quarry in Italy actually has an exploitation plan coupled with an environmental restoration plan. Especially in Tuscany, exploitation and recovery plan has to be submitted all at once based on the regional laws for the mining sector (L.R. Toscana n°35/2015) and exploitation plans can last 25 years.

According to the comprehensive definition of restoration proposed by Stanturf (2014), quarries recovery plans belong to a particular category of restoration named *Reclamation*: "Reclamation applies to severely degraded land generally devoid of vegetation, often the result of belowground resource extraction, such as mining... On such sites, more intensive management techniques are usually necessary to revegetate the site although natural recolonization can be effective". In the case of quarries this means that before planting, morphological land modelling of the site is necessary. Nowadays, in Italy quarry recovery designs are often simple works of covering mining sites followed by planting of "resistant" species, sometime using bioengineering techniques. Instead, after a careful preparation of the site, with particular attention to drainage works, it is important to choose with great wisdom the plant species that must initiate a vegetative succession able to develop autonomously. Equally important are the selected planting techniques that can also include the use of shelters, hydroretentors or hydrogels combined with nitrogen, or other methods. Above all, it is important to take care of the reforestation work for at least three or four years after planting.

Following this feasibility study, a pivotal recovery project should take effect to evaluate in practice, some new reclamation techniques suggested.

Stanturf, J.A., Palik, B.J., Dumroese, R.K. (2014): Forest Ecology and Management Contemporary forest restoration: A review emphasizing function, For. Ecol. Manage. 33, 292-323. doi:10.1016/j.foreco.2014.07.029.

# From quarrying site to geosite: a review on a possible approach to project an open-air museum as a key to preserve geological data

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Keywords: Quarry, geosite, functional recovery.

Many quarrying sites at the end of the activity are covered and re-natured through a morphological land modeling and a subsequent re-vegetation (environmental restoration). However these actions are very expensive and rarely effective, and in some cases risk to cover unique features emerging on the excavation fronts. In the last few decades, landscapes and geological features of depleted mining sites start to be considered as a resource with a public value that could attract a new generation of culturally and scientifically oriented tourists. However, to be fully effective, planning the functional recovery should take place in parallel with the exploitation activities.

Facies analysis could be a useful tool to ameliorate an overall knowledge on sedimentary stone materials, helping improving marketability, reducing the volumes of waste and collect data to plan a future open-air museum. Here we present a quarrying site in Tuscany (Italy), Poggio la Vecchia quarry. The extracted lithotype, well-known in literature as Manciano sandstone, consists of medium-coarse sands with local intercalations of conglomerates, which were deposited in shallow-water environment (see Rossi et al., 2017 with references therein). Some of the well exposed, diamond-line cut, allow a detailed analysis of textures and sedimentary structures, as well as ichnofacies, fossils, etc.; in this study, we also obtained HD ortophotoimages and a detailed morphological model using UAV flights. A huge stock of data and about 1000 detailed pictures took with a HD GPS built-in Camera were also collected and geolocated.

For its central position in the Tuscany area and the height of the mining site (more than 80m in 12 climbing walls), Poggio la Vecchia quarry represents an incredible opportunity to "read history" on every wall, of every step of the quarry. All this deserve to be preserved and turned into a Geosite. This lithotype is very stable geotechnically allowing the site to easily be converted in a visiting site, operational facilities in indoor museum areas and wasting sites in picnic areas following an environmental rehabilitation.

Exploitation and recovery plan to be submitted (L.R. Toscana n°35/2015) lasts 25 years. This timeframe is adequate to collect enough data throughout the lifespan of Poggio La Vecchia quarry.

Rossi, F.G., Madonna, S. & Milli, S. (2017): "Facies analysis applied to quarrying" a review of the possible use of sedimentology to increase knowledge and use of ornamental sandstones. Procedia Engineering, 208, 136-144.

# Italian National Parks and Mine Museums network. Re.Mi. ISPRA. Legislation draft N. 4566 date 26-06-2017

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Keywords: ecomuseum, abandoned mining heritage, restoration.

Italy is considered all around the world one of the countries with the largest mining heritage and a vast mining culture.

After closing down most mines it was not foreseen a National Plan to manage this heritage.

After many years of discontinuation of the mines, since some time, Parks and Mine museums have grown in various parts of the country with the aim of protecting and enhancing the extraordinary existing tangible and intangible mine heritage.

These mines have different management models, but all of them face the same problems such as lack of legislation and lack of financial resources.

In this context, the National Parks and Mine Museums Re.Mi. was born, promoted and coordinated by ISPRA willing to enhance the activities at a national level and develop awareness on the historical and cultural heritage.

The first important step, which was taken, is the legislation draft as a result of the territory needs, and even if this draft does not cover all the aspects it certainly is a start for innovative sustainable management of the mine heritage.

On the 2nd of October 2015 in Milan during the Expo, a Memorandum of Understanding was signed. This Memorandum stipulates the birth of National Parks and Mine Museums Network called Re.Mi. This Network is coordinated by ISPRA in association with the Ministry of Economic Development (Ministero dello Sviluppo Economico), Regione Lombardia, ANIM (National Mining Engineers Association), AIPA (Italian Association for Industrial and archeological protection), CNG (National Board of Geologists), 4 National Mine Parks and the vast majority of the Italian Mine Museums.

The need for a National Network grows during the National Mining Day, that ISPRA invents, and coordinates since 2009 as a specific need of public and private institutions to manage cultural heritage within non productive mines.

All data and info on the activities developed until today is available and can be downloaded from the site ISPRA/ReMi.

Patanè, A., Savoca, D. (2017): La Rete Nazionale dei Parchi e dei Musei minerari - ReMi - Volume UNMIG 1957-2017 - 60° dell'ufficio nazionale minerario per gli idrocarburi e le risorse - MISE.

### Mine waste management and related problems

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Keywords: mine waste, raw materials.

Extractive activities from always have accompanied men in their different evolutive steps but, at the same time, it has created big quantities of extractive wastes, often at the origin of many environmental problems. The argument of the present report aims to deepen the knowledge of what we call mine waste, that could contain also sought-after elements, with particular reference to the regulatory aspects and procedures to be followed in the event of their recovery.

The signs of this activity are scattered throughout the national territory (heaps, ponds, open pit, mining tunnels and excavation voids), often into closed or abandoned mine sites. In the past mining activities everything that was not the subject of the extraction was, obviously, considered waste, therefore it was disposed in ponds or in heaps of solid material. Their content in today highly sought-after elements (as Titanium, Scandium and Rare Earths, for example, as stated in the article *Sulcis Plan, Region for good practices and recovery of sludge treatment substances* of Sardinian Region) makes it difficult to continue considering them as waste but, rather, they should be considered as "new mines".

Current European guidelines on extractive industries are oriented in this direction; in fact, both the Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 (*on the management of waste from extractive industries*) and the Italian Legislative Decree n.117/2008, give clear indications for the extractive industries in activity phase also for the management of mine waste (Article 5 of the 2006/21/EC Waste management plan), also contemplating the possibility of their re-use/recycling. But there is a lack of clarity regarding the procedures for the management and/or reuse of mining waste, in particular for those stored in closed or abandoned structures. In this situation (closed or abandoned waste facilities) how is possible reuse or recover waste? Wath are the rules to follow?

European Commission suggests that local realities provide examples, suggestions, etc. useful for constructive comparison with other similar cases (Opinion of the European Economic and Social Committee on 'The processing and exploitation, for economic and environmental purposes, of industrial and mining waste deposits in the European Union' - *own-initiative opinion* - (2012/C 24/03). This opinion although it promotes the exploitation of extractive waste, points out that there is no assessment of the sustainability of the waste reprocessing process and calls on Member States to implement it in order to find win-win solutions.

Now the question is how to evaluate such materials potentially rich in useful elements for modern technologies and which are the most suitable regulatory guidelines to follow, also in light of the circular economy and the raw materials initiative?

Currently ISPRA is working to find guidelines for the possible recovery (recycling) of materials from extractive waste accumulated in closed or abandoned storage facilities, in order to identify possible guidelines for the use of these "waste/resources". I hope with the occasion to have aroused the interest to participate in the topic. Therefore any contribution or suggestion will be useful to find solutions in this sense, also for possible and necessary comparisons both at national and European level.

# Session S32 Cave and karst studies: from ancient to modern processes

Conveners AND CHAIRPERSONS Laura Sanna (Istituto di Biometeorologia CNR, Sassari) Mario Parise (Università di Bari) Giuliana Madonia (Università di Palermo) Marco Vattano (Università di Palermo)

# Morphology and speleothems of a cave developed in an antiformal stack of Triassic carbonates ("5 in condotta" cave, Southern Alps of Italy)

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TKeywords: riassic carbonates, Southern Alps, Hypogene cave.

The "5 in condotta" cave develops within an antiformal stack of carbonate platform facies (limestone and dolostone) of Triassic Age, south of the Valcanale village (Southern Alps, Bergamo).

The entrance is located at 1688 m a.s.l. and the cave has a total range of altitude of about 650 m and a total length of about 6000 m, reflecting the prevalently sub-horizontal orientation of the cave. The cave mostly consists of two parallel, sub-horizontal main branches cut by sub-vertical shafts and larger rooms.

Field observations included a detailed survey of the orientation of fractures as well as the orientation of fractures and major thrust surfaces. The collected data have been organized in a 3d geological model (produced with Move<sup>TM</sup> of Midland Valley Inc.) integrating surface (geological map) and underground (cave) data, in order to identify the relationships between geological setting (tectonic and stratigraphic features) and the pattern and morphologies of the cave.

Cave passages orientation creates a pattern that clearly exhibits a major tectonic control. Tectonics controls both on the orientation of the passages (which follow the main fracture systems measured in the cave) and the sub-horizontal trend of the cave, that strictly follows the thrust surface that duplicates the stratigraphic succession.

Meso-morphological forms can be mainly classified as morphologic suite of rising water flow (hypogene morphologies): rising wall/ceiling channels, cupolas (locally coalescing) and domepits are frequently observed on the roof of the sub-horizontal branches.

Morphological analyses have been coupled with a study of the speleothems. Within the cave, speleothems are distributed irregularly and their volume is generally scarce. Mineralogically, both calcite and aragonite have been identified; locally small crystals of gypsum have been observed. Micromorphological studies on thin sections show the presence of different growth stages in the speleothems. Stable isotopic analyses (the different growth stages have been sampled individually) indicate values of d18O ranging from -5 to -7 and positive values of d13C (0 to +7). Speleothems record a successive evolution of the system after the end of the possibly hypogenetic processes that produced the cave.

The study of the morphology of the cave, the attitude of the major discontinuities (fractures, faults, thrust and bedding) and the geological architecture of a complex, deformed part of the Alpine chain allowed the identification of a probable hypogenic origin of the cave (with water circulation strongly controlled by geological features), later overprinted by epigenic karst processes and subsequent development of different kind of speleothems.

The identification of a probable hypogene origin in a Prealps cave is crucial for understanding the very first beginning of karstification processes in the Southern Alps and their relationship with tectonic features.

# A geomorphologic study of epikarstic morphologies in the RNI Grotta Palombara (Hyblean Plateau) by GNSS: what controls the distribution of sinkholes?

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Keywords: sinkholes, Hyblean Plateau, RNI Grotta Palombara.

During Neogene time, the northern leading edge of the African plate collided with the southern edge of the European plate, determining the flexure of the African foreland beneath the European plate and the emergence of a large part of the Hyblean Plateau. For this reason, most of the SE Sicilian successions lack post-Messinian Salinity Crisis-Pliocene deposits (Pedley et al. 2007). This is related to the initiation of a Messinian-Early Pliocene tectonic phase affecting the Pelagian Block. This tectonic phase resulted in the uplift and development of rejuvenated, dentate horst and graben topographies across both the Maltese and Hyblean (SE Sicily) areas. These elevated Messinian successions were then subjected to subaerial karstification for several million years. This is the reason for the carved aspect of the Hyblean Plateau, characterised by impressive karstic morphologies, preserved and protected in the RNI Grotta Palombara, located 2 km north of Belvedere (Syracuse) within the SIC ITA090012. It is cut by a dense network of galleries and conduits, 800 metres in length, connected to the surface by a 12 metres deep pit-hole, 15 metres in diameter. The main epikarstic morphologies are sinkholes, sub-circular to elliptic in shape, with decametric diameter, that represent the object of this study. These sinkholes are extremely important not only as geological structures connecting the surface to the subsurface but also as environmental ecological niches. A detailed structural and geomorphological analysis has been performed by innovative methodologies (GNSS) that permitted the accurate geo-referenced mapping of the sinkholes. They are aligned and elongated along NW-SE oriented tectonic structures proving that major karstic features are located along fault planes, which act as preferential drainage patterns for groundwater circulation. Additionally, flat areas, corresponding to several orders of marine terraces (Bonforte et al., 2015), enhance the high density of sinkholes.

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# Proposal to investigate potential Atlantic-Mediterranean connection through karst conduits during the Messinian Salinity Crisis

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Keywords: drainage system, Sierra de las Nieves Karst, Messinian.

This ambitious proposal rests on the hypothesis that by characterising the palaeo-karst systems located in topographic barriers, we may quantify the contribution of underground conduits to the exchange between marine basins situated on opposite sides of the barrier, at times of different base-levels.

The aim of this project is to reconstruct the drainage system of the Sierra de las Nieves Karst (Malaga, S Spain) during the Messinian. Sierra de las Nieves (Pedrera et al., 2015) hosts one of the largest karst systems in Europe and is part of the Gibraltar Arc, a crucial topographic barrier that uplifted throughout the Miocene gradually isolating the Mediterranean from the open ocean (Capella et al., 2018).

The evolution of Sierra de las Nieves Karst during the Messinian is unclear. This stage was marked by episodes of sea-level drop, salinity gradients and significant tectonic uplift in the adjoining areas of the Sierra de las Nieves, parts of the Betic System. These changes in paleogeographic settings ultimately culminated in the so-called Messinian Salinity Crisis (Roveri et al., 2014), which lasted between 5.97 - 5.33 Ma and was terminated by the opening of the modern-like Gibraltar Straits at the Mio-Pliocene boundary (5.33 Ma).

A general consensus exists that at least one marine gateway to the open ocean must have persisted until the end of the halite stage (5.55 Ma) to allow for the large amounts of salt in the Mediterranean basin (Roveri et al., 2014). However, since surface data indicate that the late Miocene, Mediterranean-Atlantic gateways were all closed by 7 Ma (Capella et al., 2018), the location of this last connection is shrouded in mystery.

We therefore propose to perform speleological exploration at Sierra de las Nieves aimed to: i) survey the caves with terrestrial laser scanning (TLS) in order to build a 3D geomorphological model, which will potentially allow to understand the underground palaeo-drainage system; ii) sample speleothems for uranium-series dating. The age of the speleothems will provide chronological constraints for the conduits. Investigating this location could help to quantify the contribution of underground karstification to Mediterranean Atlantic connectivity, at a time when the surface gateways were closed and uplifted.

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### Secondary minerals in minothem environments

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Keywords: minothems, mine, secondary minerals.

Secondary minerals forming speleothems are called "cave minerals" and are the results of complex interactions between bedrock, circulating water, and sediments of various sources. A "speleothem" is a secondary mineral deposit formed in a cave by a chemical reaction from a primary mineral in bedrock or detritus because of a unique set of conditions therein. In Carbone et al. (2016) the term "minothems" was defined, for the first time, considering the secondary mineral concretions forming in an artificial underground void, such as a mine or any other kind of tunnel (i.e. roman aqueduct, catacomb, highway tunnel, etc.). These voids can be carved in carbonate rocks, but can also be hosted in different geological materials, such as volcanic rocks, ophiolites or granites. Minothems are the counterpart of speleothems in natural caves, and generally show the same morphologies. However, the petrographical and geological differences of the host rock can cause significant distinctions in mineralogy, colour and shape of the minothems respect to speleothems.

In this work we describe minothems and secondary minerals forming in three abandoned sulphide mines from the Ligurian (Libiola anche Reppia mine) and Piemonte region (Fragnè mine). All studied sites are abandoned and are characterised by active and intense Acid Mine Drainage (AMD) processes triggered by the supergenic interaction between sulphide-rich mineralisations and atmospheric agents. Acid Sulfate Waters (ASW) percolating inside the galleries drip through the mine roof and form numerous decorative dripstone features that coat the walls, ceilings, and floors of the mine, and grow out of muck piles creating a colourful array of white, yellow, orange, green, blue, brown and black minothems. Mine adits host soda straws, stalactites, draperies, stalagmites, columns, flowstones, gours, but can also contain pearls, rafts, coralloids (popcorn), moonmilk, and helictites. These are often composed of exotic minerals, mainly sulphates (melanterite, langite, brochantite, gypsum, felsöbányaite) silicates (allophane and crisocolla) cuprite and native copper some of which are rather uncommon because of the very special conditions that allowed for their formation in this environment.

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# Last glaciation 70 kyrs-long stalagmite palaeoclimate record from Southern Italy: implication for Mediterranean climate during glacial shifts

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Keywords: Speleothems, Palaeoclimate, Glaciation.

Stalagmites are valuable Quaternary palaeoclimate archives because: 1) cave calcite dating is highly precise and accurate; 2) geochemical (oxygen and carbon stable isotopes, trace elements, etc.) and physical (growth rate, fabric, shape and size, etc.) properties are often related to environmental changes at the surface, such as rainfall and temperature variation, shifts in vegetation type and activity, etc (McDermott, 2004; Fairchild et al., 2006; Henderson, 2006). However, records covering the last glacial period are scarce in Europe and the Mediterranean area, because the general cold temperatures and aridity did not favor the formation of speleothems in middle latitude caves. We here present a ~45 cm long stalagmite sampled in the Pozzo Cucù Cave (Apulia, Italy) that continuously grew from  $102.97 \pm 1.89$  ka to  $29.28 \pm 0.35$  ka. It follows that environmental conditions in Southern Italy, such as infiltration of rainwater in the karst reservoir and densely vegetated soils at the surface, were suitable for carbonate deposition during the whole transition toward the glacial. Carbonate formation stopped at the ~inception of the full glacial stage, probably because of the climate driven reduction of infiltrating water and vegetation CO, input in soils. Other causes, however, are taken in consideration in the paper. Preliminary carbon and oxygen stable isotopes analyses testify a significant correlation with climate changes in Greenland (NGRIP, 2004), reporting the occurrence of DO climate cyclicity (millennial warmcold climate pulses) (Dansgaard et al., 1993). This is an important indication that Southern Italy climate, representative of the whole Mediterranean area, reacted simultaneously to large-scale interhemispheric climate variations. The Pozzo Cucù record is a candidate as the longest last glaciation palaeoclimate record from the Western Mediterranean, and one of the longest worldwide.

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# Flank margin caves as signatures for past sea level fluctuations in Apulia and Sicily (Southern Italy)

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Keywords: Speleogenesis, mixing-corrosion, sub-horizontal levels.

Flank margin caves owe their formation to fresh and marine water mixing, inducing corrosion processes (Mylroie and Carew, 1990). They are very abundant on tropical islands characterized by eogenetic carbonates such as the Bahamas, Bermuda, Guam, and Cuba. Recently several flank margin cave systems have been documented in telogenetic carbonates of the Italian peninsula (Arriolabengoa et al., 2017). Generally, these caves present typical geomorphological features such as galleries with rounded cross-sections, swiss-cheese or spongework patterns, abrupt dead-endings moving away from the coastline, and horizontal notches. They lack alluvial sediments, but their entrances are often infilled with marine deposits.

This work describes three flank margin caves found in Apulia and Sicily: Sant'Angelo (Ostuni, Apulia), Pellegrino (Siracusa, Sicily) and Carburangeli caves (Palermo, Sicily). All these caves are now in vadose conditions opening along paleo-cliffs at altitudes varying from ~ 25 to 150 m asl and were carved along prominent fractures (secondary porosity). They are characterized by several sub-horizontal arrangements and show evident notches with flat roofs and spongework patterns. We found *Lithophaga litophaga* boreholes inside Carburangeli Cave, and marine deposits in the entrance of Pellegrino Cave, demonstrating important marine influences, whereas speleothems due to the seepage of meteoric waters through the host-rock occurred during subsequent stages partially covering typical flank margin cave features. Being formed by salt-fresh water mixing, they are valuable indicators of past eustatic sea levels, and if dated can allow to estimate coastal uplift rates.

### Geochemical and microbial characterization of a sulfidic cave in Santa Cesarea Terme, Italy

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Keywords: geomicrobiology, hypogenic cave, sulfidic-rich water.

Fetida Cave belongs to an active sulfuric acid system located along the Adriatic coastline (Santa Cesarea Terme, southern Apulia). It is characterized by a rectilinear and sub-horizontal branch following regional lineaments, and opening at the present sea level. Fetida Cave has a natural entrance along the cliff, opened by marine erosion, and an artificial access, used in the past to collect sulfuric mud for human treatments.

In this cave, seawater mixes and interacts with warm rising sulfide-rich groundwater, generating an extremely acidic environment causing the formation of features and deposits with peculiar geomorphology (ceiling cupolas, megascallops, rising channels) and mineralogy (gypsum, sulfur, and jarosite). Moving from the entrance to the inner part, a decrease of marine influence, together with an increase of the acidic effect due to the upwelling waters, can be observed. The amount of sulfuric acid is strongly influenced by tidal fluctuations, controlling the  $H_2S$  degassing. Concentration of  $H_2S$  in the cave atmosphere and water is highly variable and can reach 15 ppm.

Thanks to the oxidation of  $H_2S$ , providing a rich energy source, Fetida Cave hosts abundant microbial communities related to different types of deposits, visible in its inner part: i) white filamentous streamers floating on the water surface or deposited on the pool floor, ii) white creamy moonmilk deposits visible as wall crusts, and iii) worm-like vermiculations of different colors, copiously covering the cave walls and ceilings.

Here, we present the first characterization of the microbial communities within these types of deposits. Illumina sequencing approach targeting the 16S rRNA gene was combined with geochemical and microscopy (FESEM) analyses to describe the microbial diversity and biomineralization processes contributing to their formation.

### A natural geological section in southern Apulia, Italy: Vora Bosco, the deepest cave of Salento

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Keywords: geology, monitoring, hydrogeology.

Salento, the southernmost part of Apulia, is an elongated peninsula, wide some 30-40 km. Outcropping of carbonate rocks made karst the main agent in controlling the landscape in the area, with formation of many natural caves, both inland and along the coasts. The human pressure, mostly deriving from the high tourist presence during summer, has repeatedly caused severe problems of sea water intrusion in the area. Karst research in Salento may therefore be approached from many different perspectives, including, but not limited to, karst hydrogeology, speleogenesis, relationships between karst phases and sea level fluctuations, and interaction of karst caves and groundwater with human activities.

Within the framework of a project funded by Apulia Region, dedicated to control of groundwater quality and quantity, several research activities have been started at Vora Bosco (PU 1613 in the Regional Register of Natural Caves), in the municipality of Galatina (Lecce province). Choice of the cave was dictated by the presence of the water table in the deepest part of the system, located some 70 m below the ground level, an occurrence that made possible direct surveys of the groundwater. Further, the cave itself represents a natural geological section, since along its development it shows different lithologies, from the marine terraced deposits at the surface, down to the Pleistocene Gravina Calcarenites, followed by the Miocene Pietra Leccese and Andrano Calcarenites Fms. Only in the terminal pit, about 8 m-deep, the Cretaceous limestone bedrock crops out, hosting the water table. In addition to all the above, breccia deposits characterize the room from where the final sequence of pits starts.

In this peculiar cave, a variety of activities is going on: a detailed geological survey, to better define the relationships among the different lithologies; monitoring the climatic parameters in different sections of the cave; continuous control of the main parameters of the groundwater, by means of a multi-parameter probe installed in its deepest part; analysis of the time lag in the response of the water level to the recharge by rainwaters; geochemical analysis of the groundwater, in different seasons.

In this contribution we present the preliminary outcomes of the research, aimed at describing this interesting system in the general context of the Salento geology, of the karst history of the area, and with specific regard to karst hydrogeology.

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# Deep water in Apulia Region: monitoring and exploration in the karst environment of "Inghiottitoio di Masseria Rotolo"

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Keywords: karst, monitoring, hydrogeology.

The "Inghiottitoio di Masseria Rotolo" is one of the two sites of Apulia Region where karst phenomena allow direct investigation (that is, through cave explorations and surveys) of the groundwater. It is the deepest cave in the Region, with a maximum depth of -324 m below the ground (cave access at 300 m a.s.l.). The cave system is located within the karst polje called "Canale di Pirro", in central Apulia, elongated in N-E direction, with outcrop of the Cretaceous limestone bedrock, covered discontinuously by thin terra rossa deposits. The cave develops entirely in this limestone formation and shows very impressive underground karst landforms and speleothems.

This recent and important discovery is the object of a scientific project, still in progress, funded by Apulia Region. A series of speleological and diving expeditions were carried out to try to discover the whole cave system, but it has not yet been completely explored and the activity is still ongoing. The system monitoring is guaranteed by means of a multi-parameter probe in the water table, and a series of sensors to detect the main climatic parameters of the cave environment; further, geological and geomorphological data useful to characterize this complex karstic system are being collected and examined. During the first phase of water sampling, a multi-parametric profile with depth below water table was performed where groundwater is intercepted by the cave. Today these data are being analyzed, and will be processed by means of a mathematical model to study surface water and groundwater interaction. The second phase of sampling has been scheduled for late June 2018.

Water samples, collected at different depth in the cave, provide biological and chemical parameters needed to the groundwater characterization. Specific chemical parameters are detected in order to investigate the water quality in the karst system, and the burden of anthropic impact in a so remote and undisturbed underground habitat as well; other parameters, on the other hand, are taken to investigate the deep-water origin and water flow pathways. In addition, isotope analyses could be addressed to assess age and origin of deep water into the cave.

This contribution describes the first monitoring activities carried out during the project with particular attention to the hydrogeological and chemical quality of groundwater and surface water. These, together with geological, morphological and hydrogeological characteristics, will help researchers to understand the complex dynamic of karst areas.

*Acknowledgment*: work funded by Protocollo d'intesa con Regione Puglia per l'attuazione dell'art. 45 "Interventi per esplorazione dei fenomeni carsici", comma 1 della L.R. n. 45 del 30/12/2013.

# A review of the issue "karst-bauxites" in Istria and Northern Dalmatia (Adriatic Carbonate Platform) - a new scientific paradigm and new challenge in the study of karst lands

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Keywords: Karst bauxites, Ferralitic weathering, Incongruent dissolution.

The Adriatic Carbonate Platform (AdCP) is a large Mesozoic platform with carbonate deposits of variable thickness between 3000 and 5000 meters which has ended his existence in the regional emergence between the Cretaceous and the Paleogene with the tectonic deformation and flysch deposits. In the new structural models, a certain number of stratigraphic discontinuities of variable duration is indicated, especially marked by breccias and bauxitic deposits. When contained in limestones the bauxites are defined "karst bauxites. The karst bauxites are now locally distributed at different levels of different ages - developed in Mesozoic, expecially Jurassic and Cretaceous, Paleocene and Early Eocene and in different structures with specific mineral characteristics. The NW part of the arch along which AdCP is developed consists of Istria and northern Dalmatia Islands (Krk, Cres) in a successions of carbonate deposits (limestones and dolomitic limestones) with a thickness of about 2000 m of Jurassic to Eocene age with the final covering of the Foraminiferal Limestones and therefore of the Flysch. Carbonate deposits can be roughly distinguished into three large sequences and at least in additional four or five minor sequences. This sequences, identifiable by stratigraphic gaps, represent the testimonies of important emersions (subaereal exposition). There are different theories on the origin of karst bauxites. The intent of this article is to summarize views and modern knowledge derived from recent studies on the phenomenon, limited to bauxites of Istria and Northern Dalmatia islands (Croatia). Over the past three decades significant results were achieved regarding the geochemical analyses, stratigraphy and geological characteristics. But there are recurring questions of the scientists: method of deposition and mineralogical differences. Deposits occur in various forms: lens, breccia, oolites, veins, layers in pockets. Sometimes deposits are housed in karstic depressions, covered by other limestones. There are not always any precise references and stratigraphic correlations between karst bauxites and the original aluminosilicates rocks, for example the rocks derived from volcanic eruptions or from the emergencies of ophiolitic fragments. The bauxite deposits have different composition, and mineralogical differences are also present in the same outcrops. You can find, in the same sample of rock, hematite and goethite as well as gibbsite and boehmite. The diaspore, present in Istria, is rare in northern Dalmatia. Other common rare mineral phases are kaolinite, chlorite, magnetite, ferrihydrite, tourmaline, zircon and anatase. In Central Istria (Minjera) marcasite and pyrite are also present along with radionuclides.

These rocks formed by transport and accumulation of residual clay derived from the alteration of alluminosilicates rocks on land through weathering and neomineralisation. Anyway the essence of bauxitisation is the incongruently dissolution transforming the minerals aluminosilicates rocks in Al and Fe oxides - hydroxides rich residues.

### How Big is a Cave?

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Keywords: Fractal, Vivofit, Cave.

This work is inspired to a Badino suggestion, to list the Italian rank of the biggest caves. It is not something I thought being a good job being inconsistent and with 4 basic issues: Data volatility, Untrue declarations, Missing uniformity of surveying techniques, and the last point is related to a philosophical issue about this article, what it means big? The answer to this question has been resolved in the time building 2 lists: the deepest and the longest caves of the world. Badino pointed out interesting interpretations, where for the first time a fractal index is evidenced. This work start from this point, and is focused on the biggest Italian caves having as a goal to use a single number to define the importance of a cave. I start to consider the dimension of a cave using an index seen on some newspaper, this index is multiplying the depth with the extension. But it fails in the case of very deep caves with small extensions or with very extended caves with insignificant depth. So something more accurate must be found. One idea could be to list the cave using an easy calculation of the ideal triangle area that is covered by the cave in the mountain. A table with this calculation related to the most important Italian cave is listed. I don't feel this approach respectful of the complexity of a cave in its relations with the mountain where it fits. We could use a fractal measure of the cave development. This parameter allows to have in a single number, the degree of fitting of the cave inside the mountain. An explanation on how to proceed in this work, and which available free sw in the mkt to use is provided. At the end of the calculation, a list of Italian caves ranked by fractal dimension is provided. A comparison of this result with other very big International caves is given, in order to present how difficult it to compute the fractal dimension in absence of a standardized available counting programs. Some comment on the meaning of using the fractal dimension to measure the size of a cave are listed, including the fact that with this approach we will have de density of the cave in the mountain, and so probably its exploration potential, but not again how it fit inside the full volume of the mountains. A further parameter is mentioned, thanks to the high diffusion of the watch physical parameter meters. Using those systems, on multiple cavers, it would be possible to define a human power parameter in Joule per hour, indicating a new way to measure the cave with its relation with the caver. The use of this parameter gives important information to the caver that wish to enter in an unknown cave, providing an objective measurement of the degree of difficulty of the system. In the final part a comment on the difficulties to collect all the needed survey from several groups in Italy, and a "strange picture "obtained graphing depth with development of the Italian cave. An interpretation of the graph is commented.

### Structural control on water circulation in the Bossea karst system (S Piedmont, Italy)

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Keywords: structural setting, karst aquifer, vadose zone.

The Bossea karst system is located in the Ligurian Alps of southern Piedmont (Italy). Its water feeds the Corsaglia river, one of Tanaro river main tributaries. The cave is nearly a kilometer long and represents the terminal portion of a larger karst system. This system can be subdivided in two segments: an upper and a lower one. In the upper segment the underground river (called Torrente Mora) flows along a canyon carved into a Mesozoic meta-carbonate sequence. The lower segment, on the other hand, cuts meta-volcanics rocks and is characterized by large rooms and massive collapses. The water resurfaces in the Corsaglia river from a set of springs.

This project couples structural geology analysis with hydrochemical and hydrological investigation of the karst system to understand the speleogenesis and water circulation in the vadose zone above the cave. The geological and structural survey within the cave and in the surrounding surface outcrops revealed a complex structural setting caused by disharmonic defomation between the Permian meta-volcanics and the meta-carbonate sequence above. Low-angle shear zones and related folds are localized in proximity to the disharmonic contact. In addition, steeply dipping strike-slip shear zones with a E-W to ESE-WNW orientation cut both the meta-volcanics and meta-carbonate sequences. These structures probably formed during the main Alpine deformation and subsequent events, as highlighted also by previous works at the regional scale (d'Atri et al., 2016). The geological/structural survey also revealed that vadose water circulation developed mainly along the folded bedding interfaces that act as preferential pathway for the percolating water. Fracture clusters at slipping beds terminations may provide additional secondary pathways and through-sequence connectivity. The most important structural feature that controls the development of the cave and conduit water circulation is the disharmonic contact between the Permian meta-volcanics and the above Mesozoic meta-carbonate sequences, along which Torrente Mora developed.

D'Atri, G., Piana, F., Barale, L., Bertok, C. & Martire, L. (2016): Geological setting of the southern termination of Western Alps. Int. J. Earth Sci. 105, 1831-1858.

### The November 2016 flood event in the Bossea cave system, Southern Piedmont (Italy)

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Keywords: Karst aquifer, hydrochemistry, flood monitoring.

Bossea cave (S Piedmont) hosts an underground river (called Torrente Mora), flowing at the contact between Permian metavolcanites and Mesozoic limestones, fed by some small tributaries that drain the vadose zone (Vigna et al., 2017a). The cave hosts an underground scientific laboratory since the late 70s and managed by the Bossea Scientific Station of the Alpine Club of Cuneo and the Central Scientific Committee of CAI in collaboration with the Polytechnical University of Turin. The scientific laboratory has studied the cave for almost 40 years and more recently it has developed a continuous monitoring network for both hydrologic and hydrochemical parameters of groundwater. Between November 21-25 2016 heavy rainfall (357 mm) caused one of the strongest historical floods recorded in Bossea Cave, similar to the one happened in 1996 (Vigna et al., 2017b).

Both Torrente Mora and the vadose zone were monitored during this recent extreme flood event. The underground river and the small tributaries were equipped with multiparametric devices and data loggers for the monitoring of water level (L), temperature (T) and electrical conductivity (EC). An automated water sampler collected 4 times a day from November 20 to December 2 in the river, whereas samples were taken immediately before and after the flood in the other points. Major, minor and trace elements and rare earth elements (REE) were analyzed.

Dripwater chemistry displayed small changes during the flood event, while T, L and EC changed significantly. EC increased shortly before the flood peak, while T increased contemporaneously with water level. These data point to an impulsive behaviour of the unsaturated zone where the infiltrating freshwater mobilized part of the water stored in the vadose zone. Torrente Mora showed strong changes during the flood in both chemistry and hydrological parameters. Its water chemistry is strongly controlled by the carbonate host rock and by the amount of water-rock interaction that is function of fresh water input.

Vigna, B., Peano, G. & De Waele, J. (2017a): The karstological subterranean laboratory of Bossea cave (N Italy). Proc. 17th Int. Congr. Spel. Sydney 1, 447-451.

Vigna, B., Fiorucci, A., Nannoni, A. & De Waele, J. (2017b): Vadose zone hydrogeology in the Bossea cave system (Southern Piedmont, Northern Italy). Proc. 17th Int. Congr. Spel. Sydney 2, 222-225.

### Speleogenesis of Grotta della Molara cave (north-west Sicily)

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Keywords: Mixing-corrosion, phreatic speleothems, uplift rate.

In this paper we present the first results of a geomorphological study aimed at the reconstruction of the genesis and evolution of the Grotta della Molara cave, developed at ~100 m a.s.l. in the south-eastern slopes of Castellaccio Mt., north-west of Palermo. The geomorphological setting of this area is characterized by large coastal plains limited by high coastal paleo-cliffs on Mesozoic limestones. A succession of Pleistocene marine terraces occurs from sea level to about 200 m a.s.l. (ISPRA, 2013 and references therein). The cave is 220 m long and 32 m deep and is characterized by an unique passage developed in Triassic platform limestone along a SW-NE fault zone. At the entrance of the cave there is a large roofless room which walls show several levels of tidal notches at different altitudes and a large band of lithophaga holes. Geomorphological analysis in and outside the cave recognized different erosion and deposition forms linked to vary processes. Scalloplike indentations and small phreatic passages due to corrosion by mixing of salt and fresh water cut the cave walls; cupolas and forms of condensation-corrosion processes are widespread; corrosion forms linked to guano deposits are visible too. The cavity is characterized by the presence of very large breakdown blocks, different types of carbonate vadose speleothems (soda straws, stalactites, stalagmites, columns, gours, etc.), phosphate crusts, and phreatic speleothems (encrustations and cave clouds) growing along horizontal levels at and under the former water table. Analysis of the erosion features and deposits suggests a quite complex genesis and evolution of the cave linked to corrosion processes by mixing of freshwater and seawater and successive gravitative processes in a vadose environment. Fluctuations in global sea level combined with uplift of the area led the cave to go through phreatic phases with mixing dissolution processes, vadose phases characterized by breakdown of large volumes of rocks and speleothems deposition, partial flooding phases with deposition of phreatic speleothems, and periods when direct connection with the sea occurred. Comparing the cave features with surface morphologies, the eustatic sea-level curve, and uplift rates of the area, it was possible to suppose a chronological evolution of the speleogenetic events starting from the cave origin occurred likely at the Middle Pleistocene transition.

### Karst features of the Favignana island (Sicily)

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Keywords: Favignana island, Sicily, karst Geosites.

The island of Favignana is the main island of the Aegadian archipelago, which also includes the island of Marettimo and Levanzo. From a geological point of view, the Egadi archipelago represents the emerged part of the submarine mountain chain connecting the Sicilian-Maghrebian Chain with the Tunisian one. The island consists mainly of Mesozoic carbonate rocks, and secondly of Quaternary rocks, which have undergone, from the early stages of their emergence, a widespread process of karst corrosion, both on the surface and in depth. This highlights a marked karst morphological in the landscape imprinted with karren and cavities in the hinterland and along the coast, the latter also characterized by numerous sea caves. To study this interesting geomorphological context a research project on the karstic aspects of the island was carried out by the CIRS Ragusa, also having the purpose of documenting the presence of geomorphological features of scientific and / or aesthetic relevance to be proposed as Geosites under the Regional Law 25/2012, for their protection and fruition with minimum impact. With these objectives the study was structured in three phases, with a series of field-trips for the surveying of the surface karst features, the exploration and surveying of different type of caves and for the surveying of sea karren along the coastal belt. The surveying of the surface karst morphologies has allowed for the highlighting of the widespread presence of corrosion forms in the dolomites and dolomitic limestone of the Upper Trias-Lias period, constituting the lithostructural framework of the Santa Caterina ridge. Among the 22 surveyed and documented caves (classified as epigenetic, singenetic, hypogenic, structural and littoral caves), the study has highlighted, for different features: the Ciacca Niura, as the deepest and widest cave of the island; the *Grotta d'Oriente*, an interesting cave for its spectacular flowstone formations; the Grotta delle Pecore, the Grotta della Ucceria and the Grotta Faraglione, classified as flank margin caves, present in the western sea paleo-cliff of Capo Grosso - Faraglioni promontory and, among the documented paleo-sea caves, the Grotta dell'Acqua, located at 85 m asl, which presents a particular paleontological interest due to the discovery of fossil coral incrustations on the walls, to be studied for their paleoenvironmental and paleogeographical implications for the knowledge of the geological history of the central Mediterranean area. Finally, the surveying of sea morphologies along the coastal belt of the island has highlighted the presence of a varied and rich range of marine karren as a result of the erosion and corrosion processes, both physical and biological. On the basis of the results obtained, the establishment of seven Geosites were proposed, made up of six karst caves and one Stone forest area, according to Regional Law 25/2012, for their valorization and protection.

### Environmental characterization of Sardinia show-caves: first approach for a LCA study

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Keywords: Cave environmental, cave management, cave micrometeorology.

A very attractive and potentially competitive tourism sector in Sardinia is those of the show caves. The island is currently the Italian region with the largest number of tourist caves and the karst cavities equipped for visits represent, in fact, already today an important economic resource, attracting thousands of visitors each year. These sites, often located in the inland areas, as well as along the coast, are a valid alternative to seaside tourism and an interesting attraction to the internal territory of the island, with obvious benefits also for other areas of naturalistic and archaeological interest scattered throughout the island hinterland.

Moreover, unlike the leading sector of the Sardinian tourist industry, inevitably linked to the summer period, due to the mild climatic conditions of Sardinia, speleological tourism is mostly usable even in the other seasons, as most of the caves can also be visited in winter.

It seems therefore essential to put a greater effort to promote this resource through an innovation of the product and encourage an increase in the percentage of visitors who reach Sardinia even or just to directly visit the scientific features of its caves. However, despite the Sardinian show caves are highly appreciated for their beauty and for their peculiarities, most of them are not yet sufficiently known and valued.

In this framework, the environmental characterization of Sardinia show-caves has been carried out with the aim to produce a systematic definition and classification of the touristic services and to evaluate the associated environmental impacts, specific features and limitations.

For each of the 16 Sardinian show-caves, their natural resources, monitoring system and management have been analysed. This study intends therefore to deepen the knowledge on some aspects of the Sardinian speleological sector, providing new tools for service innovation. The characterization of these show-caves is the first approach for the application of the Life Cycle Assessment (LCA) method to the touristic service offered by show caves. This methodology allows to assess the environmental performance of the service, to improve and promote sustainable processes and green marketing and finally to provide a sound basis for informed decisions on cave management.

### Groundwater geochemistry of the Sisine coastal karst system (Central-East Sardinia, Italy)

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Keywords: groundwater, coastal karst, Gulf of Orosei.

The Sisine karst system is one of the coastal underground drainage networks of the Gulf of Orosei that develops within the Mesozoic carbonate succession of coastal Supramonte, along the contact with the underlying impermeable Paleozoic basement. The recharge area of this cave system is located in the Su Canale plateau, which represents a structural high of the monoclinal, dipping towards the sea. The major sinkholes are Lovettecannas and Murgulavò caves that drain the allogenic recharge of small depressions. The typical morphologies of these caves are wide voids that increase their size with depth, with volumes incompatible with the available discharge. Dissolutional features are lacking and parts of these vadose passages are sometimes developed for several metres in granite or metamorphic rocks. Their outflow, hypothesized towards the underground coastal springs, has been recently demonstrated by the direct observation of dye tracer in the Beltorrente Cave, an underwater spring that opens 500 m north of Sisine beach, along the coastal cliff of Gulf of Orosei.

This karst system has been recently investigated to determine the geochemical signature of its groundwater. In particular, the water sampling was carried out in the Lovettecannas and Murgulavò streams and at the Beltorrente spring. In addition to the analysis of major elements, a series of periodic measurements of discharge and in situ physico-chemical parameters (pH, conductivity, total dissolved solids, alkalinity and temperature) have been carried out.

The preliminary data analysis show that the small stream of Murgulavò has a relatively high water temperature for the altitude at which its entrance opens (900 m asl) and equal to  $12.1 \,^{\circ}C$  (internal air temperature of  $12.4 \,^{\circ}C$ ), with conductivity of 0.29 mS/cm and a pH value of 7.6. In the Lovettecannas stream the pH values remain relatively basic (> 8.2), the conductivity around of 0.30 mS/cm and the temperature ranges from about 8  $^{\circ}C$  in the passages close to the entrance to higher values which increase with depth reaching 11.6  $^{\circ}C$  at the CinCin Hall at an altitude of 630 m asl.

Groundwater geochemistry have been confirmed to have a calcium bicarbonate character, as result of a water-rock interaction that mainly involved rock portions with a magnesium composition (dolomitic lithotypes) even though the monitoring of physico-chemical elements shows clearly heterogeneity in the hydro-chemical feature of the drainage network that suffers the seasonality of the external input, which mitigates its effects gradually penetrating towards the deeper part of the aquifer.

### Preliminary data on CO, monitoring in the Murge (Apulia, S Italy)

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Keywords: carbon dioxide, monitoring, cave climate.

The concentration of some trace gases in cave is documented to have higher values with respect to the outside atmosphere. Partial pressure of carbon dioxide is one of the main parameter in cave due to its control in speleothem deposition and speleogenesis. Its concentration could depend on soil activity in the cover, or disaggregation of organic matter, but mostly is originated by the karst process itself through the nucleation of calcium carbonate. Recently this gas has been proposed as a key in local carbon cycle at short term scale as sinks and sources for atmospheric  $CO_2$ .

With the purpose to understand the anomalous high concentration observed in the Murge of Apulia, this work reports the preliminary results of the  $CO_2$  monitoring performed in the underground atmosphere of 5 caves in this karst region, (Castellana, Salto, Calzino, Torre di Mastro, and Abate Eustasio), monitored in January 2018 Air CO<sub>2</sub> concentration was measured as mixing ratio using a Non-Dispersive Infra-Red spectrometer NDIR (Zenith), with a range 0÷10,000 ppm and an accuracy of ±50 ppm. As the concentration of this gas in air masses is dependent of its water vapour content, temperature and relative humidity were also recorded. In the Castellana Cave the monitoring was performed continuously for few days using a NDIR datalogger (Perfect Prime: range 0÷10,000 ppm; accuracy ±50 ppm) which recorded CO<sub>2</sub> concentration every 10 minutes.

The preliminary results show an increase in CO<sub>2</sub> concentration with depth. It ranges from typical value of cave environment to level proximal to soil concentration. The partial pressure of CO<sub>2</sub> in Torre di Mastro at 40 m in depth from the surface reaches value >10,000 ppm (temperature 12.5 °C - 100%). In Castellana Cave the monitoring lasted for 1 day in a passage close to the public trail, with concentration around 800 ppm, and some peaks during the night. Here the temperature was 14.0 °C and relative humidity never reached saturation (85%) probably due to the artificial ventilation of the cave. Spot measurements were also performed along the touristic path with values ranging between 1,000 to 1530 ppm. The carbon dioxide content in the Salto Cave had typical cave values (from 2000 to 2800 ppm). Only the final shaft showed CO<sub>2</sub> concentration > 10,000 ppm (temperature 18.2 °C - 100%). The lowest value was recorded at the Abate Eustasio Cave with pCO<sub>2</sub> ranging between 900 ppm at the bottom of the entrance and 1,000 ppm in the inner cave passages (temperature 16.2 °C - 100%). On the other hand, the Calzino Cave showed the highest and dangerous CO<sub>2</sub> concentration that suddenly rose few meter below the entrance (16.2 °C - 100%), reaching 12,700 ppm in the shaft at -10 m and 36,000 ppm further inside at -20 m in depth (a shaft never explored for this reason). This CO<sub>2</sub> value seems not related to physical parameter such as temperature and relative monitoring. Further investigation could clarify this pattern.

# Biomediated SiO<sub>2</sub> mobilization and deposition of amorphous silica speleothems in non-thermal subsurface environments

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Keywords: quartz weathering, amorphous silica, bacterial diversity.

Silicon is among the most common elements of the Earth's crust. The role of microbes in silica mobilization has been investigated mainly in hydrothermal environments, whereas the mechanisms behind the formation of biologically mediated silica deposits in non-hydrothermal quartz-dominated ecological niches are largely unknown. While in hydrothermal natural systems the formation of amorphous silica deposits (sinters) is facilitated by high temperature solutions allowing for silica precipitation at the discharge point, the deposition of opal in epigenic geochemically stable environments at low T and neutral pH is uncommon because quartz dissolution kinetics are usually too slow to cause saturation. Here, we describe a microbial dependent process occurring in the world's largest quartz-sandstone cave (Imawari Yeuta Cave, Venezuela) that causes dissolution of quartz and precipitation of amorphous silica at low constant temperature (i.e., 17 °C) and acidic to neutral pH (i.e., 5 - 6). Illumina-MiSeq analyses indicate that non-phototrophic bacteria orchestrate the process boosting quartz dissolution to obtain nutrient and bio-essential elements. The dissolved silica eventually re-precipitates forming an array of speleothems, including layered stromatolite-like microbial-rich deposits. This finding shows that chemotrophic bacterial communities can drastically enhance quartz weathering and silica mobility through geochemical controls on the microenvironment, with implications in the comprehension of the silica cycle in the subsurface. These results open new insights into the relationship between silica and biomediated precipitation processes, a crucial step for understanding the early life on Earth (i.e. Archean stromatolites) and for the search of potential biosignatures in silica-rich deposits on Mars.

### Semi-submerged sea caves in the central Mediterranean sea: the Geoswim database

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Keywords: coastal karst, Geoswim, coastal geomorphology, Mediterranean Sea.

The Mediterranean Sea is bordered by about 23.000 km of rocky coast that host several types of scenic coastal landforms, such as sea caves, sea stacks, arches, etc. An overview of the researches on these landforms in the Mediterranean area was provided by Furlani et al (2014). Sea caves are one of the most characteristic and fascinating coastal landforms along rocky coasts. In the Mediterranean Sea there are thousands of sea caves that develops along the coastline. Sea caves represent a basic landform both for studies on coastal processes, such as sea level change or coastal karst, and as touristic attractor in coastal areas.

A sea cave is composed by one or more chambers originated by different processes and are totally or partially occupied by the sea. Waves and marine processes contribute to the genesis and development of sea caves.

In this work, we present field data collected on semi-submerged sea caves surveyed during the swim and snorkel campaigns of the Geoswim project (Furlani, 2012) in North-Eastern Adriatic Sea (NE Italy, Slovenia and NW Croatia), Mt. Conero area (Marche, Italy), Gozo and Comino islands (Malta), Egadi Archipelago and Ustica Island (Sicily, Italy), Capo Caccia (Sardinia, Italy) and the island of Paros (Greece). Till now, the database contains data of about 122 semi-submerged caves and represents the only large-scale database of this kind of data.

Field data were joint to published data or sea cave registers. The study areas are mainly composed by carbonate rocks, in fact 83% of the studied sea caves develop on limestones or dolomites, while the remaining 17% on volcanic rocks.

From a first analysis of field data, there is a heterogeneous distribution of all the sea caves. Some areas show higher concentration of sea caves rather than other areas. This is due to local structural, lithological and sea conditions. During the surveys at Favignana Island (Egadi Archipelago) a new sea cave was found out. This discover has a precious ecological significance as the cave represent an ideal habitat for the monk seal.

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## Session S33

## The contribute of the quantitative and qualitative hydrogeology in the study and management of the water resources

Conveners And CHAIRPERSONS Francesco Fiorillo (Università di Sannio) Sergio Rusi (Università "G. D'Annunzio" Chieti-Pescara) Maria Filippini (Università di Bologna)

## Hydrogeochemical anomalies before the 2016 Mw 6.0 and 6.5 earthquakes in Italy: new data and possible relationship with deep CO, influx

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Keywords: earthquakes hydrology, groundwater, water table.

Hydrological and hydrogeochemical changes caused by pre- and co-seismic processes have been reported for thousands of years. Transient hydrogeochemical anomalies are increasingly becoming commonly recorded before  $M \ge 5.0$  earthquakes at distances between 20 and more than 200 km from the earthquake epicenters. The 2016 Amatrice and Norcia earthquakes as well as the related sequence were anticipated by hydrogeochemical anomalies, in particular, since April 2016 an increase of As and V contents was recorded in groundwater from springs monitored in the Sulmona area about 70 km to the southeast of the epicentral area, and in a spring located within the epicentral area. On November 2016, these elements recovered their original very low concentrations. We considered these geochemical anomalies as reliable seismic precursors of the case-study for a dilatational tectonic setting. To validate these parameters as reliable seismic precursors and, consequently, to constitute an effective predictive tool, it is necessary to move from observed site-specific anomalies in groundwater to the comprehension of the geological and geochemical processes driving these anomalies. A pre-seismic and co-seismic elemental contribution from the bituminous-asphaltic residues and/or hydrothermal fluids could be hypothesized. However, neither additional metal (e.g. Ni, Mn) nor TDS or water isotope anomalies, which should be consequential of hydrocarbon decomposition and fluid mixing, respectively, have been detected. Consequently, a different possible source of the anomalies the steady characteristics of groundwater flow and the simultaneous increase of selected metal ions has been evaluated. Chemical and isotope models reveal that the abnormal content of As and V and the concomitant lowering of the boron isotopic ratios up to +2% may be due to mineral desorption (e.g. from iron oxides and/or clays). Based on these data, the geochemical processes that led to the cited metal element increase in groundwater would be related in a new perspective on possible deep CO, input. Furthermore, new data on the isotope ratios of the dissolved boron show potential application of the  $\delta^{11}$ B parameter as potential precursory signal of earthquakes, at least in the study area.

### Geochemical groundwater modifications connect to central Italy earthquake of 2016: Torbidone case (Norcia plain, Italy)

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Keywords: Hydrogeochemistry, Earthquake, Apennines.

In 2016 Central Italy has been affected by a long and strong seismic sequence starting on August 24<sup>th</sup>. The strongest shock of the sequence (MW=6.5), with epicenter about 5 km NNE of Norcia and hypocenter at a depth of about 8 km (Chiaraluce et al., 2017), occurred on October 30<sup>th</sup> 2016 After this shock, several springs located in the Norcia Plain experienced important discharge variations. The Torbidone spring, dry since 1979 Norcia earthquake (MW=5.9), was re-activated with a very large flow rate and other two springs located nearby, S. Martino and Praterella, sensibly increased their discharge. Starting from August 2016, these three springs and the main springs of the neighboring Umbria-Marche carbonate aquifers were sampled, with the aim of contributing to the evaluation of the causes of the perturbations and to investigate the system evolution. For each spring, temperature (T), pH, Eh, electrical conductivity (EC) and total alkalinity were determined directly in the field and major anions and cations, dissolved gases, water and dissolved carbon isotopes were determined in laboratory.

The main springs of Norcia Plain are characterized by temperature ranging from~7.5 to 12.1 °C, pH from ~7.30 to 7.90 and EC from 247 to 649  $\mu$ S/cm. The compositions of all sampled waters are mainly Ca-HCO<sub>3</sub> type with variable contents of SO<sub>4</sub> and Mg, excluding Triponzo thermal water which shows a Ca(Mg)-SO<sub>4</sub> composition, T of~30 °C, pH of~6.90 and EC of~2400  $\mu$ S/cm (Beddini et al., 2018).

Torbidone, S. Martino and Praterella springs show higher Mg-SO<sub>4</sub> content, associated with relatively higher salinity, with respect to other non-thermal springs of the area. The Mg-SO<sub>4</sub> content showed, however, different variations in time for the three springs. These differences can be ascribed to the fact that these springs are fed by different groundwater systems; this is also highlighted by the isotopic groundwater compositions, showing a narrow range of variations during time for Torbidone spring and a wider range for S. Martino and Praterella springs. These geochemical features suggest the possible occurrence of different groundwater systems, the pathways and interactions of which are still under investigation also by means of on the hydrogeological and structural point of view.

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## From acid-rock drainage to acid-mine drainage: extreme contamination in waters at the Furtei Au-mine (Sardinia, Italy)

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Keywords: Acid mine drainage, Mining, Environment.

The weathering of sulfide-bearing mineral deposits, exposed either by natural erosion or by mining to oxygen and water, can produce natural acid-rock drainage (ARD) and mining-related acid-rock drainage (acid mine drainage, AMD), respectively. The composition and extent of acid drainage is highly variable, depending on many factors, such as the composition of ore bodies and related host rocks, climate, mining operations and processing (Nordstrom and Alpers, 1999). Due to the low pH and high concentrations of contaminants, acid drainages can severely degradate surface and groundwater systems, as well as soils.

At Furtei (Sardinia, Italy), a high-sulfidation epithermal gold deposit consists of pyrite and enargite with minor amounts of luzonite, tennantite, and chalcocite. The oxidized cap mainly consists of iron oxy-hydroxides, gypsum, jarosite, halotrichite and scorodite. The gold deposit was exploited by open pit from 1997 to 2003. The Au and Ag were recovered from oxidized ores by cyanidation. Sulfide ores were processed by flotation to recover Cu concentrates. Total production was about 4 t of Au, 6 t of Ag, and 1500 t of Cu (Cidu et al., 2013).

Pre-mining conditions showed waters (flow <0.1 L/s) with pH down to 2.3, a typical example of ARD characterized by high salinity (26 g/L) with predominant sulfate (20 g/L) and very high amounts of dissolved contaminants (in mg/L): Al 2000, Fe 1700, Mn 35, Cu 29, Zn 11, Ni 4, Co 3, Cr 1, As 0.4, and Cd 0.1 (Cidu et al., 1997).

During exploitation and after the mine closure, the number of sites with contaminated water increased. Contaminated waters showed pH and chemical compositions similar to those observed under pre-mining conditions, but much higher concentrations of Cu, Zn, As and Cd, respectively up to 180, 97, 5, and 1.7 mg/L (Da Pelo et al., 2009; Cidu et al., 2013). The seepage from the tailings impoundment is collected in a well and back pumped into impoundment. The highly contaminated water in the open pits and drainages from the pyrite-rich waste dumps may flow downstream from the mine under heavy rain periods and pose a hazard to agricultural areas.

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#### Hydraulic connection between fractured and porous aquifers in glacial valleys

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Keywords: Fractured aquifer, Glacial valleys, Dolomiti Mountains.

Mountain regions are of fundamental importance as water resource areas and, with the present climatic trend, it is expected to see a significant increase of stress on these water resources (Viviroli et al., 2011), therefore it is important to know and understand their behaviour, to better manage the available resource, especially in drought conditions.

The hydrogeological unit of the "Pale di San Martino Dolomitic group" hosts a main fractured and karstified aquifer, hydraulically connected with glacial and alluvial porous aquifers of the valleys. The fractured aquifer is underlain by clayey aquiclude and the aquifer/aquiclude limit outcrop induces perennial springs. Where this limit is covered by detrital deposit, a hydraulic connection between fractured and porous aquifers could be expected.

The aim of the ongoing studies is to define the hydrogeological role of the alluvial and glacial complex, to detail the connection between fractured and porous aquifers and to explain discharge variations in the riverbed springs fed by these aquifers. This has been done by analysing existing geological and hydrogeological data, new data from monthly discharge measurements, the available seismic lines (Caielli and de Franco, 2011) coupled with reconstruction of riverbed longitudinal profile.

The study site corresponds to the San Lucano Valley, where about 38% (2.5 m<sup>3</sup>/s) of the whole "Pale di San Martino" hydrogeological unit discharge (about 6.5 m<sup>3</sup>/s) flows out (Lucianetti et al., 2015).

Preliminary results show that: i) a decrease in discharge happens as the alluvial and glacial complex thickness increases; ii) at the knickpoint in the riverbed longitudinal profile, a large increase in river discharge happens as the water table is intercepted by the topography; iii) a second large increase is verified at the end of the valley, where the aquiclude of the fractured aquifer outcrops in correspondence to the ancient threshold of glacier forcing the groundwater outflow from the porous aquifer.

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### Hydrogeological setting and groundwater hydrochemical characteristics of the Lauria Mounts northern sector (southern Italy)

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Keywords: carbonate hydrostructure, hydrogeology, hydrochemistry.

The carbonate hydrostructure of the northern sector of the Lauria Mounts is located in the southern-western part of the Basilicata region (southern Italy) and holds strategic groundwater resources. In the last decades, the rising of freshwater demand due to the population needs, the agricultural and industrial water consumption, requires to identify possible alternative available water resources, considering also the groundwater climate change impact, land use variability and groundwater pollution. In this perspective, the effective quantification and the hydrochemical assessment of the available groundwater resources are the starting point for the correct characterization of the available groundwater resources, aimed at the delineation of the adequate management and proper protection actions. The study area, characterized by a evident geological-structural complexity, is represented by a high-structural, consisting of the Meso-Cenozoic calcareous-dolomitic succession, referable to the Alburno-Cervati-Pollino Unit, constituting the monoclinals of the Calabrian-Lucanian border, confined by the Miocene clayey-marly flysch. The articulated geostructural setting strongly conditions the carbonate hydrogeological structure. The hydrostructure geometry, oriented in the WNW-SSE direction, consists of two aquifers, bordered laterally by major faults, and characterized by subsurface boundaries that define different groundwater flows: Lauria and La Spina - Zaccana substructures, both distinct by the presence of numerous springs exploited and not, some of them characterized by important groundwater discharges, and representing a notable water resource for the area and the entire region. Several groundwater samples were collected and analyzed to characterize the physico-chemical parameters, such as temperature, pH, electrical conductivity, total dissolved solids, cations (Ca2+, Mg2+, Na+, K+), anions (HCO3+, Cl-, SO3+, NO3+) and trace elements (Al, Fe, Cd, Pb, As, Zn), and to assess the hydrogeochemical and the rock-water interaction processes. The analytical results highlight an excellent groundwater quality and indicate that the concentration values in all groundwater samples are below the permissible limits for drinking and irrigation purposes. The chemical composition, chiefly controlled by calcite and dolomite dissolution phenomena that take place during the rock-water interaction processes, shows the dominance of the calcium-bicarbonate (Ca-HCO<sub>2</sub>) hydrochemical facies, coherently with the presence of the limestones and dolomites and the hydrogeological setting of the aquifer system. In particular, the water samples of the springs belonging to the Lauria aquifer have lower values in magnesium, in line with the lithology characterizing the substructure (limestones), with respect to the springs of La Spina - Zaccana aquifer, whose the interaction phenomena with the dolomites constituent the substructure, lead the magnesium at slightly higher concentrations.

#### Effects of groundwater rebound in the metropolitan area of Naples (southern Italy)

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Keywords: groundwater rebound, groundwater flooding, ground uplift.

Environmental and hydrogeological problems arising from groundwater mismanagement have been recorded in numerous world urban and rural areas (Allocca et al., 2016). In the urban hydrogeology literature, the case study of alluvial aquifer system in the Naples metropolitan area is certainly one of these.

Literature data show that from 1950 to 1989, the aquifer mismanagement has caused: a) the overexploitation (with withdrawal rate up to about 6,0 m<sup>3</sup>/s) of the alluvial plain aquifer system and a progressive decline of the water table levels (up to -2.0 m b.s.l.), which ended in 1989 (Allocca and Celico, 2008), and b) a decay of hydrochemical quality of groundwater by the increase of nitrate, iron and manganese concentrations.

Groundwater quality deterioration and urban transformation processes led to a sharp reduction and deactivation of groundwater pumping for drinking water, irrigation and industrial uses and, consequently, since 1990, a continuous phase of groundwater rebound occurred (Allocca and Celico, 2008). The latter phenomenon has had strong socioeconomic and environmental impacts on urban and rural contest in the last decades, causing groundwater flooding in subway tunnels, buildings, agricultural land and archaeological sites (Allocca et al., 2016), as well as ground deformations with consequent damage to structures and infrastructures.

The present study aims to investigate some groundwater rebound problems in Naples metropolitan area, by: i) coupled analysis of multi-temporal hydrogeological and DInSAR data for the 1989-2013 period; ii) multitemporal mapping of the buildings and agricultural soils affected by groundwater flooding.

Results show a generalized increase of groundwater levels, with a rising velocity up to 2.2 m/yr, and analogues trend is observed in ground deformations. Interferometric data show ground uplift, with a magnitude up to about 40 mm, caused by the increase of water pore pressure in the aquifer system, following to groundwater rebound. Groundwater flooding affects some buildings and agricultural soils, and this phenomenon is characterized by very heterogeneous temporal-spatial distribution, because it's conditioned by natural and anthropogenic factors (Allocca et al., 2016).

Results obtained demonstrate how the aquifer mismanagement and wrong urban planning can increase geohazards in urbanized environments, and opens new perspectives in assessment, mitigation and management of a new risk not considered by Italian legislation.

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### Hydrogeochemical and isotopic studies of the middle Valley of Volturno River (Campania Region)

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Keywords: groundwater, isotopic analyses, Campania.

The drought occurred in recent years (e.g. in 2017) imposes a deep knowledge of the characteristics of the aquifers and of the relationships between surface waters and groundwater, also considering the possible over-exploitation of the groundwater resources.

The area of the study concerns the wide valley crossed by the Volturno river (groundwater body of the "Middle valley of the Volturno river") located in southern Italy. In the eastern sector, the valley is constrained by a narrowing carbonate slopes of the M. Maggiore (to the north) and of the M. Tifata (to the south). The tectonic relationships between M. Maggiore and M. Tifata are very complex. In the valley, at the base of the carbonate slopes, pyroclastic deposits are associated to detritus from the carbonate slopes while, in line with the river network, they are replaced by alluvial deposits linked to the Volturno's enlargement. These sediments form the shallow aquifer of the valley and they have, according to the size of elements and the grain-size assortment, a permeability which varies from low to medium-high. However the main aquifer of the plain corresponds to the carbonate substratum which is found at variable depths below the alluvial-pyroclastic deposits.

The area is characterized by a Mediterranean rainfall regime with a single maximum in winter (November) and a dry summer (August). The average rainfall ranges between 1350 mm/y and 1050 mm/y. The temperature in the valley ranges between 9° C in January and 25° C in July, while on the mountain ranges between 3° C in winter and 20° C in summer.

Along the southern sector of the valley, quite close to the river, there are two well fields (Q tot  $\approx 51 \times 10^6 \text{ m}^3/\text{y}$ ); other two well fields are located at the foot of the above mentioned mountains (Q tot  $\approx 47 \times 10^6 \text{ m}^3/\text{y}$ ).

The piezometric surveys of the wells of the valley and the interpretation of the chemical and isotopic analyses (D, <sup>18</sup>O) of the well fields and of the river, allowed a better understanding of the relationships, at different times of the year and for different drought/wet years, between the groundwater flow in the carbonate mountains (eastern sector of the valley) and between the groundwater resources tapped from the various well fields and the river.

## Quantitative hydrogeology of the shallow aquifer of S. Eufemia Lamezia plain for the management and protection of water resources (central Calabria) - Preliminary results

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Keywords: S. Eufemia Lamezia plain, shallow aquifer.

In Calabria, excluding the "organic study of groundwater resources" (Cas.Mez., 1978), the "Water Protection Plan" (SOGESID, 2009), some works on limited portions of territory, there are no quantitative hydrogeological studies. Therefore, the present study, currently in the preliminary phase, aims to contribute to the hydrogeological knowledge of the region and in particular, of the shallow aquifer of S. E. Lamezia plain characterized by a multi-layered aquifer (Cuiuli, 2012; 2015). This plain, lies in the Tyrrhenian sector of the "*Graben of Catanzaro*" (Amodio Morelli et al., 1976) generated by sub-vertical faults with a left lateral strike-slipe component (Gulla et al., 2005). In the study area, there are many abusive wells without data. However, for authorized wells, are available: stratigraphy, static and dynamic level, flow rate. Therefore interpolating (Kriging) the stratigraphic data, was derived the clayely substrate map and the depth (b) of the aquifer. Lowering in wells [DS] has been determined from groundwater levels. Transmissivity has been estimated with the Logan formula [T=1.22 Q/DS] (Celico, 1986); the Permeability [K=T/b]. The storage coefficient has been estimated with the Logan (Cuiuli, 2015). The hydraulic gradient [i] has been graphically determined (Celico, 1986) from the piezometric map (Cuiuli, 2012).

From this preliminary estimate, the hydraulic parameters of the aquifer are:

 $1,5 \ge 10^{-4} > T > 6,8 \ge 10^{-3} [m/s];$   $1,8 \ge 10^{-6} > K > 5,3 \ge 10^{-4} [m/s];$   $2,5 \ge 10^{-4} > S > 3,8 \ge 10^{-4};$  0,7 > i > 0,1

that are variable from the hinterland to the coast, supposedly for the granulometric heterogeneity of the alluvial lithotypes of the plain.

In conclusion, this study aims to provide an estimate of the main quantitative hydrogeological parameters of the shallow aquifer of S. E. Lamezia plain, for the protection and correct management of water resource.

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### The integrated vulnerability map of S.E. Lamezia plain (Calabria) as a qualitative assessment tool to support territorial development

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Keywords: S. Eufemia Lamezia plain, shallow aquifer, vulnerability map.

The S. E. Lamezia plain, characterized by a multi-layered aquifer (Cuiuli, 2012; 2015) lies in the Tyrrhenian sector of the "Graben of Catanzaro" (Amodio Morelli et al., 1976). The intrinsic vulnerability map of the shallow aquifer of the plain (Cuiuli, 2013), has highlighted vulnerability degrees variables from medium to very high, moving from the hinterland to the coast. In this context, the anthropic activities present can generate negative impacts on groundwater. Therefore, according to the APAT Guide Line (2001) have been mapped: the real and potential pollution producers; the potential pollution intakes of the aquifers; the pollution preventers and/or reducers; the main pollution subjects.

Overlaying these elements on the intrinsic vulnerability map was returned the integrated vulnerability map. This last one correlates the danger centers with the intrinsic characteristics of the study area. This cartography territorializes the types of pollutants according to the anthropic activities existing on the plain and the predisposition of the aquifer, in qualitative terms, to intake and disperse a pollutant into the environment.

In conclusion, this study aims to provide a contribution to the definition of potential pollution risk scenarios in the plain, returning a qualitative assessment of the shallow aquifer vulnerability that can be used to support the planning tools for a correct management of the resource and for prevent degradation and pollution of groundwater.

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## Hydrogeological effects of the 2016 earthquake on the groundwater circulation of the Norcia area

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Keywords: Hydrogeology, Earthquake, Apennines.

On October 30<sup>th</sup> 2016, in Central Italy, an MW 6.5 earthquake, with a normal fault mechanism NNW-SSE trending, occurred at a depth of about 8 km. The epicenter was located about 5 km NNE of Norcia. The seismic sequence caused several significant changes of groundwater flow in the stroked area (Petitta et al., 2018).

Right after the October  $30^{\text{th}}$  event, the Torbidone spring, located in the Norcia Plain and dry since the 1979 Norcia earthquake (MW=5.9), was suddenly re-activated. Its discharge continued to rise almost continuously during the following months, reaching the highest value (1.68 m<sup>3</sup>/s) in May 2017; afterwards, the discharge began to lower and in December 2017 it was halved (0.76 m<sup>3</sup>/s), reaching, in April 2018, a minimum value of about 0.66 m<sup>3</sup>/s. The depletion curve follows the exponential Maillet equation with a depletion coefficient of  $3.1*10^{-3}$  days<sup>-1</sup>.

The Torbidone spring feeds the Sordo River, the discharge of which significantly increased after the earthquake. Although this variation is probably linked to the input of other limestone massifs located East and South-East of the Norcia Plain, part of this increase is due to the contribution of Torbidone and other smaller springs, located in the Norcia Plain, the discharge of which increased after the earthquake. The reconstructed structural setting suggests the hypothesis of a hydraulic connection between the Torbidone spring and the eastern aquifers hosted within the Meso-Cenozoic carbonate sequence, with the groundwater flow path coming from the deepest part of these aquifers. In particular, a connection can be supposed with the lowest aquifer of the sequence (basal aquifer) hosted in the Calcare Massiccio and Maiolica limestone formations of the Sibillini Mountains. This hypothesis is supported by the fact that the Torbidone water is enriched in SO<sub>4</sub> and Mg; this could be due to a chemical interaction with the Triassic dolomitic-evaporitic rocks on which the basal aquifer lies.

In particular, the co-seismic displacement of about 1.5 m of the Mt Vettore-Mt Bove fault system (Chiaraluce et al., 2017) coupled with an increase in permeability may have facilitated the groundwater transfer from the Mt. Vettore basal aquifer to Torbidone spring.

Tracer tests performed just before the seismic sequence (June 2016) allowed to highlight a connection between the Sibillini Mountains area and the Sordo River. Further tracer tests, performed by April 2018, should allow to define whether and how the groundwater circuits have been modified by the earthquake.

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### New insights on advanced redox zonation of aquifers using multivariate geostatistics: the San Pedro Sula case study

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Keywords: Redox zonation, Multivariate geostatistics, Euthrophicated surface-water.

The incorrect land use and wastewater management represent anthropogenic pressures on the environment, which can create heavy euthrophication conditions in surface-water. When surface-water/groundwater relationships exist, the organic matter produced in the euthrophicated streams can be transferred into the aquifer, triggering redox processes (i.e. Terminal Electron Accepting Processes, TEAPs). These hydrogeochemical processes provoke severe groundwater quality modifications (e.g. Mn and Fe solubilization), that complicate its exploitation and management. The definition of the redox zonation of aquifers represents an effective tool for the identification of the pollution sources and for the conceptual model refinement, when remediation strategies and groundwater management plans need to be implemented.

The study area is the San Pedro Sula aquifer (north-western Honduras), which is a multi-layer alluvial aquifer characterized by well-known surface-water/groundwater interactions and by heavy euthrophicated streams. Here, high concentrations of Mn and Fe have been found in the aquifer (Di Curzio et al., 2016).

Although the redox processes are dynamic reactions, the redox zonation is generally aimed to identify homogenous zones within an aquifer characterized by a predominant TEAP (McMahon & Chapelle, 2008). To overcome this methodological approach, the Multi-Collocated Factorial Kriging (MCFK) (Sollitto et al., 2010) has been applied to chemico-physical parameters and analytes, diagnostic of the redox processes (i.e. temperature, pH, turbidity, Mn, Fe, NO<sub>3</sub>, NH<sub>4</sub>, PO<sub>4</sub>). These parameters have been measured in 93 wells, both in the wet and dry season. In addition, the distance from the surface-water has been selected as an auxiliary variable, essential to perform the MCFK, because the eutrophicated streams have been considered one of the pollution sources.

The MCFK results show a short range variability, highlighting a strong relation between Mn concentrations and redox processes, due to the organic matter transfer from heavy polluted surface-water to the aquifer. Simultaneously, the relation between Fe and turbidity can be due to a fine colloidal phase, developed when different redox conditions of groundwater mix up in the wells. At a wider range, Fe seems to be related with redox processes, near the other pollution source detected in the northern San Pedro Sula alluvial plain.

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## Estimation of effective recharge in hard rock aquifers based on spring discharge monitoring during the low flow season

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Keywords: hard rock aquifer, effective recharge, summer discharge monitoring.

Hard rock aquifers (or discontinuous aquifers) are commonly intended as igneous or metamorphic rocks with very low primary porosity and a significant however discontinuous and strongly anisotropic secondary porosity (i.e. fractures) due to tectonic stresses and weathering. In some cases, the term "hard rock aquifer" is well suited also for sedimentary fractured rocks. This is the case of the turbiditic formations in the Northern Apennines (Italy), that represent the most valuable groundwater reservoir in the region. In such cases, the quantification of water resources hosted in the hard rock aquifers becomes of paramount importance. We propose a method to quantify the effective recharge occurring within a spring recharge area in a hard rock aquifer setting when only spring discharge monitoring during the low flow season (summer) is available. An empirical relationship was found between the average annual discharge of a spring and its average summer discharge, starting from a large database of 11 hydrologic years of discharge monitoring on more than 80 springs. Such relationship is linear on a log-log scale and changes according to the Maillet's recession coefficient. The average annual flow rate obtained from summer monitoring data (i.e. the average summer discharge and the Maillet coefficient) is considered as a proxy of the effective recharge occurring within the spring recharge area. The proposed method was tested both in turbiditic and ophiolitic hard rock aquifers in the Northern Apennines in different hydrologic years, providing an overall accuracy in the range of  $\pm 15\%$  with respect to the actual annual average spring discharges. Thus, this is a promising tool to support the application of hydrologic balances in hard rock aquifers. However, further tests should be carried out in different hard rock aquifer settings in order to form a basis for more realistic expectations about the overall validity of the method.

#### Hydrogeological and hydraulic features of upwelling flux feeding karst springs

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Keywords: upwelling flux, hydraulic head, ascendant hydraulic gradient.

The upwelling groundwater flux has been investigated by deep piezometers in a spring area characterized by alluvial deposits covering a karst substratum in Southern Italy. The piezometers are of varying depth located in a flat area. They have been monitored for a long period (about 40 years), and when measured, a good relationship between spring discharge and hydraulic head was observed.

The local upwelling groundwater flux has been deducted by the increasing of the hydraulic head in depth, which allows the estimation of ascendant hydraulic gradient and groundwater velocity during the dry and wet seasons. A specific analytical solution has been used to estimate the zone involved by the ascendant flow, and could also be used in other spring areas. Some physical and chemical characteristics of spring water have been collected, including the radon (<sup>222</sup>Rn) activity, to support the phenomenon of the ascendant flux. The man geological and hydrogeological features leading to ascendant flux in karst environments is also discussed for some areas of Southern Italy, where many springs are affected.

The ascendant water flux which feeds the springs belong to a wide hydraulic phenomenon involving wide areas and deep portions of aquifers. It is always connected to specific hydrogeological conditions, coming from tectonic and geomorphologic evolution. In a karst environment, the ascendant flux can be particularly developed because of the carbonate dissolution along the shorter flow lines, characterized by the higher hydraulic gradient and forming karst conduits as well as allowing the water flux to siphon under no-karst terrains. This phenomenon is still poorly quantified, as deep hydraulic measurements are generally missing.

A specific equation has been provided to estimate the area involved by the ascendant flow, and appears a useful tool to define the discharge zone of springs, and, thus, a more efficient local planning in order to correctly manage and preserve the quantity and quality of groundwater resources.

## Treatment of arsenic contaminated groundwater: a case study in the south of Sila Massif (Calabria, Italy)

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Keywords: Arsenic, contaminated groundwaters, nanofiltration treating.

The occurrence of high arsenic concentration into worldwide groundwater is one of main environmental problematic of present day. In water systems, As can occur mainly as oxyanions of trivalent  $(As^{3+})$  and pentavalent (As<sup>5+</sup>) inorganic forms (Smedley & Kinniburgh, 2002) as the result of water-arsenic minerals interaction. These minerals are mainly sulphides: arsenopyrite (FeAsS), orpiment ( $As_2S_2$ ), realgar ( $As_2S_2$ ) and arsenian (As-rich) pyrite (Fe(As,S)<sub>2</sub>). This study reports the data of 3 arsenic contaminated springs located in the Catanzaro province (southern Sila Massif, Calabria, Italy) where Hercynian and pre-Hercynian gneiss, granite and metapelite belonging to Calabride complex, outcrop (Van Dijk et al., 2000). In the 3 collected groundwaters (S1, S2 and S3) the following As concentrations were detected: 60, 120 and 430 ppb, respectively. Several studies have shown that oral exposed to arsenic is the cause of many diseases and cancers and for this reasons the WHO drinking water guideline for As in groundwater has been set to 10  $\mu$ g/L (WHO, 2001). For reaching this acceptable concentration value, the three samples were treated by membrane process as nanofiltration (NF) (Figoli et al., 2016). The experiments were conducted at different operating pressures (3 bar, 7 bar, 11 bar and 15 bar) using a NF laboratory scale system and 4 different types of commercial membranes named DK (proprietary thin-film), CK (cellulose acetate), NP030P (Polyethersulfone) and HL (Polyamide) respectively. For each experiment, permeate flux and arsenic rejection were evaluated. The results have shown that HL membrane is the most performing, although all the investigated membranes, except the NP030P, highlighted an As concentration under 10 µg/L. Moreover, the best results were obtained for the S1 and S2 water samples. These findings confirmed as NF processes can be successfully applied to decontaminate natural polluted waters allowing the potable use after the treatment.

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## New statistical methods for the geochemical characterization of surface waters: the Tiber River basin case study

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Keywords: surface waters chemistry, compositional data.

The Tiber River has its source in the Mount Fumaiolo at an altitude of 1268 m above sea level. After flowing through Tuscany, Umbria and Lazio, it enters, at the end of its course of 409 km, the Tyrrhenian Sea near the city of Rome. The Tiber River catchment is the largest river basin in central Italy, draining an area of 17,156 km<sup>2</sup> and is characterized by the terrigeneus deposits in flysch facies in the upper part, the carbonatic Apennine ridge towards south-east and the potassic and ultrapotassic volcanic complexes in the south-western part. In 2017, during several sampling campaigns, 160 water samples belonging to both the Tiber River and the main tributaries were collected and analyzed for dissolved major species and several trace elements. In this study the chemical composition of waters is investigated using new statistical methods such as the Compositional Data Analysis approach. The compositional nature of geochemical data is well known in literature (Aitchison, 1986; Egozcue & Pawlowsky-Glahn, 2005), consequently the concentration of solutes should be considered in a compositional context (Buccianti et al., 2008). The results are graphically displayed using biplots to evaluate the geochemical variables responsible for data variability. According to the method proposed by Filzmoser et al. (2012), multivariate outliers for compositional data are also highlighted and their locations shown on map. Furthermore the robust Mahalanobis distance between pairs of multivariate observations in a compositional context is calculated in order to detect changes in the Tiber River waters composition going downstream. This method allows to evaluate the similarity among samples and relate the changes in water composition to possible environmental drivers such as geology, geomorphology, precipitation, land use as well as to the anthropogenic impact.

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### Stable isotopes (H, B, C and O) and chemical evidence of deep-seated fluids in the waters emitted from "Macalube di Aragona" mud volcanoes (Sicily, Italy)

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Keywords: Mud Volcanoes, Stable Isotopes, Diagenetic Processes.

The main chemical and isotopic (H, B, C and O) signatures of waters emitted from the "Macalube di Aragona" mud volcanoes area (Sicily, Italy) were determined with the aim of identifying the origin of the expelled fluids.

Mud volcanoes (MVs) are geologic structures representing significant natural emissions of oil and gaseous hydrocarbons from buried sediments. Waters associated to MVs are brackish or brines having variable and sometimes extreme chemical and isotopic composition, depending on their origin (mainly seawater) and on the post-deposition processes they have undergone (evaporation, leaching of evaporate rocks, destabilization of gas hydrates, dewatering of clays and so on).

The "Macalube di Aragona" is the largest MVs area in Sicily. Nonetheless, this area has not been studied in detail neither as regards the mechanisms of the formation of mud volcanoes nor as regards the origin and the nature of the fluids.

The most significant geochemical features observed in the collected fluids are: 1) Na and Cl are the dominant dissolved components; 2) salinity is about 60-70% lower than seawater; 3) all the ionic ratios have been modified with respect to seawater; 4) very high alkalinity (up to 63.6 mM) and exceptionally high B contents (up to 189 ppm); 5) depletion in deuterium and strong enrichment in oxygen-18 with respect to seawater and 6) unusual positive signature of dissolved inorganic carbon ( $d^{13}C_{TDIC}$  up to +24.6‰).

Based on these findings, a model of the origin of porewaters has been proposed. It assumes that fluids, the original composition of which is similar to that of seawater, were entrapped in sediments during deposition. Afterwards, during late Cenozoic age, warm, low-medium salinity fluids were diagenetically formed within the deepest levels of the Sicilian accretionary prism. These newly formed fluids had mixed at depth with porewaters strongly altering pristine pore waters composition (salinity, ionic and isotope ratios).

Water isotope signature seems to point to that freshening of pore water is probably due to minerals dehydration and smectite transformation into illite. The latter diagenetic process should lead also to the increasing of Na<sup>+</sup> and depletion of K<sup>+</sup> as well as to the shifting of the D/H and <sup>18</sup>O/<sup>16</sup>O ratios of water in the way it was observed.

High alkalinity seems to be due to the dissolution of residual  $CO_2$  related to secondary biogenic methanogenesis and anaerobic biodegradation.

Finally, based on the estimated geothermal gradient in the Sicilian Neogene accretionary complex (18-22°C km<sup>-1</sup>) the probable source of water has been inferred at depth between 2 and 7 kilometers along the detachments.

#### The benefits coming from groundwater monitoring in urban areas, the case of Rome

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Keywords: Urban hydrogeology, groundwater flow, groundwater quality.

The largely invisible world of groundwater is involved in many aspects of a city life: water supply systems, sewage, surface-water features, the health of plants and trees, flood potential, and drought events. Recently, groundwater has been recognized as a cornerstone in the resilience of the cities. Under this perspective, mapping and monitoring groundwater and surface water resources represents a fundamental step for optimizing the urban water system and minimizing water consumption and deterioration.

In the city of Rome, even if at the beginning of its lifetime the local historical springs provided the water supply, nowadays most of drinking water supply derives from springs located far from the city, and is delivered to population through the aqueduct network. Even if, currently, there are not specific issues related to water quantity, however, the Rome municipality is dealing with many groundwater related problems. Some examples are: pollution, relationships between poor quality streams and aquifers, natural background levels of dissolved elements and compounds, differential settlements in streams valleys, subsidence and salinization as well as groundwater flooding in the coastal aquifer. Consequently, the sustainable groundwater management in towns poses, not only scientific challenges, but also technical, socio-economic, cultural and ethical.

The impacts of groundwater within a specific urban area depend both on its geographical location and the economic status of the city or even the country. While for cities of developing countries the main interests are therefore water quantity and quality, in developed countries, urban groundwater is posed in economic and environmental terms. Use and managed recharge of groundwater may reduce pressure upon conventional freshwater supply sources. On the other hand, not using this groundwater may lead to flooding and structural damage to underground structures (underground railway systems, basements, underground parking areas, etc.).

The knowledge base today is stronger in Rome, thanks to the new hydrogeological map and the new monitoring network implementation, and there are many advanced technologies not only for resources protection, but also for a correct management in a greater urban resilience perspective. This is particularly true when technologies like Managed Aquifer Recharge and Storage are considered to solve specific urban floods issues as well as blue and green infrastructures.

The existence of a wide groundwater monitoring network allows also to make possible the constant updating of hydrogeological data as well as possible investigations about the potential presence of contaminants out of the known polluted sites.

#### The acidic waters in Italy: a brief overview

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Keywords: Central-Southern Italy, acidic waters, volcano-hydrothermal fluids.

Acidic waters are relatively common and associated with extremely variable geological settings. These peculiar fluids may cause serious threats to ecosystems and trophic chain. Consequently, as they impact the environment, their distribution and physicochemical features deserve to be investigated. The present study is aimed at providing a brief overview on the Italian acidic waters based on literature and unpublished data. Geogenic low-pH fluids are commonly found in: i) volcanic and hydrothermal environments and ii) ore body-bearing areas.

The western and inner sector of Italy, along the Apennine belt, is known to be interested by thermal anomalies, mostly related to Quaternary-to-present magmatism to which the presence of ore bodies is often linked. Among the most famous geothermal and volcano-geothermal systems, the following areas are noteworthy: i) Larderello and Mt. Amiata (Tuscany) and ii) Neapolitan and Aeolian volcanic systems (Campania and Sicily, respectively). All these localities present a large number of hydrothermal manifestations, mainly including thermal water and gas discharges, and are characterized by the occurrence of strongly acidic fluids (pH  $\leq$  2). In these areas, bubbling and boiling pools frequently occur as the result of the interaction of deep-sourced gases with shallow aquifers. The chemical composition of such fluids usually pertains to Ca-SO<sub>4</sub>, NH<sub>4</sub>-SO<sub>4</sub> or Na-Cl facies depending on the different features of both the uprising fluids and the geological substratum on which the considered emissions are located. Temperatures are generally between 15 and 96 °C, whilst TDS values range from <1 to around 30 g/L. High metals concentrations are frequently measured. Nevertheless, in the peripheral areas of these geothermal systems, those groundwater bodies, that are used as drinkable water supplies, can be also locally affected by the sporadic presence of acidic to slightly acidic springs (pH values from ~4 to 5.85) which is reasonably ascribed to gas-water interaction processes likely to occur in correspondence of fault zones.

Alternatively, acidic waters can be released as AMD l.s. (*Acid Mine Drainages*), occurring downstream of the major mining districts (e.g. Colline Metallifere, Tuscany; Libiola, Liguria; Sardinian mining districts). Such fluids typically show pH values as low as 2.5, extremely high metals contents and a chemical composition dominated by Na-SO<sub>4</sub>, Ca(Mg)-SO<sub>4</sub>, and/or Mg(Ca)-SO<sub>4</sub> waters, prevalently due to an oxidative dissolution process of S-bearing minerals. More rarely (e.g. in Mt. Amiata area,  $3^{rd}$ class-mercury ore ever exploited worldwide), these waters can be encountered whenever a punctual portion of a shallow cold aquifer is intercepted by an uprising CO<sub>2</sub>(H<sub>2</sub>S)-rich gas phase, escaping from abandoned mine boreholes.

An effective protection of eco-systems, for the two above discussed settings, could be achieved by: i) reliable hydrogeological studies and ii) well-designed remediation techniques, respectively.

#### Recharge process of a dune aquifer in the roman coast

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Keywords: Coastal aquifer, Monitoring network, Tiber delta.

The urban development plan of left bank of the Tiber river Delta preserved a 9 km<sup>2</sup> stretch of dune belt with a monumental coastal pine forest (Castelfusano forest), nowadays part of a natural reserve managed by Municipality of Rome.

The forest was largely destroyed by a first huge fire in July 2000 and by a second one in August 2017. After the 2000 fire a reforestation project involved the installation of a monitoring network of 20 piezometers to check the groundwater depth and its degree of salinization. It is indeed known that there is a strong link between the forest dune ecosystem and the persistence of fresh shallow groundwater. Less well known is the relationship between the forest persistence and the groundwater recharge process.

By examining series of water head measurements and chemo - physical parameterization carried out from 2002 to today, the current research aims to analyze the effect of 2017 fire on the recharge process. In this work the first results are shown, in particular those about the reconstruction of the recharge and the groundwater flow conceptual models. To get information about the 2017 fire effects, we are waiting the end of the 2018 rainfall recharge.

The data have been carried out occasionally over the years. Continuous data sets collected once a month are available for all piezometers from April 2011 to May 2012 and from May 2016 to June 2017. A daily continuous monitoring started in 2014 in one piezometer, increasing up to six piezometers in the flowing years until today. In April 2016 chemical analysis of water of all piezometer was also done. A termo pluviometric station is present on the south eastern edge of the Castelfusano dune.

An initial interpretation of available data indicated the sand dune hosts a shallow aquifer (2 - 3 m bgl) recharged by zenithal infiltration. Moderate salinization processes (E.C. values between 2 and 4 mS/cm) characterize this aquifer, with a discontinuous spatial distribution. Only in the deepest layer of one piezometer, high salinization values (8.5 - 11.5 mS/cm) were found. The chemical analysis confirmed the salinization can be attributed to increase of Na and Cl concentration.

Seasonal piezometric maps were produced and the groundwater flow path was reconstructed in detail. By using standard calculation criteria, the recharge period was identified at monthly scale and compared with monthly water table fluctuations. The comparative statistical analyses of the daily data about the water table fluctuations and rainfall, allowed to identify the faster response time dynamics. The spacialization of these results suggested different responses to the recharge in different sector of the aquifer, on the basis of the forest cover remained after the 2000 fire. Once all recharge data will be analyzed, the inferred rainfall/recharge cycle will be also compared with that post 2017 fire scenarios.

## Assessing long-term projected impacts of climate change and socio-economic factors on regional groundwater system: Adda-Ticino basin case study

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Keywords: regional groundwater flow modelling, climate change impacts, groundwater usage predictions.

Climate change would strongly influence the water cycle in a long term period, potentially impacting the groundwater system, both in highly urbanized areas- where water is largely abstracted for public and industrial purposes - and also in rural ones- where groundwater could be used to mitigate crop water stresses which are supposed to increase in future (Alberti et al., 2016a). Therefore, the potential long term consequences of climate variations on groundwater resources need to be accurately investigated accounting for a wide combination of climate change scenarios and socio-economic trends, directly impacting on groundwater use. From this perspective, numerical groundwater flow modelling represents a strong tool for planning future groundwater management policies. In this study, a calibrated groundwater numerical model (MODFLOW2000) developed for the hydrogeological basin Adda-Ticino in Lombardy (Alberti et al., 2016b) is used to run long term scenarios in order to define the groundwater levels distribution at the end of the century. Simulated scenarios are defined through the combination of projections of climatic variables influencing meteoric recharge (rainfall and temperatures) with different groundwater usage projections (i.e. variation of public and private withdrawals and recharge from irrigation networks). Local climate projections are obtained from the outcomes of a Regional Climate Model, based on greenhouse gases emission scenarios (Representative Concentration Pathways - RCPs) defined by the International Panel on Climate Change (IPCC). Groundwater usage scenarios are determined on the basis of socio-economic factors (i.e. population growth, trend in water consumption, industrial and agricultural activities). The results of the projected scenarios simulations allow assessing future trends in groundwater level variations and estimating the main items of the groundwater balance (i.e. discharge to Ticino, Adda and Po rivers, water exchanges between aquifers) at 2100. The comparison between the different projections, here evaluated, aims to highlight possible future vulnerabilities and risks for the groundwater resource in the densely urban areas (Milan metropolitan area) and the rural ones (south of Milan), comprised in the model domain. This could help regional water authorities in implementing optimal groundwater management policies and undertaking actions addressed to face groundwater future issues.

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## Similarities and differences on recharge phenomena between some karst systems of southern Apennines (Italy)

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Keywords: groundwater recharge, endorheic areas, karst springs.

The southern Apennines are typified by several karst areas representing an important source of drinking water; particularly basal springs of karst areas, with discharge of several thousand liters for second, are tapped by aqueduct companies in order to supply population water demand.

Karst areas are characterized by highly permeable rocks (limestone) providing large amounts of groundwater recharge which are estimated considering three carbonatic structure of southern Italy: Matese, Terminio, Cervialto. The main features joining three karst systems are endorheic areas which have a predominant role in recharge processes, because the rainfall reaching the closed areas don't provide runoff and completely contribute to spring discharge. Hydrological analysis was carried out estimating the annual groundwater recharge and considering temperature and rainfall data for thirty years (1970-1999). In order to define annual scale recharge model, the regression line of annual mean values of different ground-elevated rain gauges and thermometers was found (Fiorillo et al. 2015; Fiorillo & Pagnozzi 2015). The parameters on which the model relies on (total meteoric afflux, temperature, actual evapotranspiration, effective meteoric afflux) are computed using GIS tools, building a grid for each one (Pagnozzi et al. 2017).

For Matese and Cervialto massif similar recharge coefficient for open areas was found due to similar morphological features, while Terminio massif shows open areas groundwater recharge higher than Matese and Cervialto, even if the values are absolutely comparable (Fiorillo et al. 2015; Fiorillo and Pagnozzi 2015). While for Cervialto and Terminio the water pumped for hydroelectrical exploitation is missing (Cervialto) or negligible (Terminio), for Matese massif this antropic activity affects the recharge processes both in natural endorheic areas and artificial lakes of Gallo and Letino (Fiorillo & Pagnozzi 2015). Nevertheless the analysis of annual groundwater recharge testified how the closed areas play a predominant role for karst aquifer recharge, contributing to feed basal springs through karst net (shafts, swallow hole) that allow the water drainage towards basal springs. For this reason endorheic areas should be preserve because its are particularly vulnerable to pollutants, triggering a fast drainage of fluids towards springs.

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## Geochemical and isotopic survey of the surface waters from the Arno River Basin (central Italy): new insights on the sources of the N-bearing species by using nitrogen and oxygen isotopes

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Keywords: Arno River, Surface Waters, Nitrate.

River systems are sensitive to anthropogenic contamination and among the main contaminants N-bearing species play an important role as they can predominantly be released by different and variable sources such as fertilizers, domestic and agro-zootechnical wastes. In the last decades, several European directives in environmental purview have introduced both a restrictive use of these compounds in agriculture and more accurate monitoring activity. Consequently, generally speaking, their content has significantly reduced. However, contamination of N-bearing in surface waters is still matter of concern. In the last few years, geochemical and isotopic surveys of surface waters from the Arno River Basin, the third major basin in Italy, have shown that the N-bearing species concentrations are often critical, particularly in the central and western part of the river course. In this study, a new survey is presented and includes the geochemical features of the Arno River and the main tributaries. The contents of NH<sub>4</sub>, NO<sub>2</sub> and NO<sub>3</sub> are up to 4,77 mg/L, 8,72 mg/L and 62,5 mg/L, respectively, suggesting that no significant improvements in the water quality have occurred when these data are compared with those already published. Despite the fact that concentrations provide useful information about the status of the Arno Basin surface waters no clues can be obtained about the sources and processes that affect the N-bearing species. This can tentatively be achieved by investigating the isotopic composition of nitrogen and oxygen. Isotopic data with a new analytical approach are here presented for both nitrate and, for the first time in the Arno River, nitrite. These data suggest that domestic wastes and natural fertilizers do still play a key role in the contamination of the Arno waters, while nitrite is apparently associated with oxidation processes of ammonium.

## Graphical-numerical methods to investigate geochemical variability in natural waters under CoDA (Compositional Data Analysis)

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Keywords: Compositional data analysis, Isometric log-ratio transformation, Langelier-Ludwing diagram.

This study is focused on detecting and interpreting the different sources that are able to generate chemical variability in surface waters by using the CoDA (Compositional Data Analysis) approach (Aitchison, 1982). Geochemical data pertain to the constrained simplex sample space, since each concentration represents the proportion of a given total. Therefore, with the aim of exploring the spatial variability and stability of D geochemical variables (as parts of a composition) in the correct sample space, the method recently proposed by Martin-Fernandez et al. (2017) was applied by extracting D-1 principal balances (isometric log-ratio real coordinates) from a compositional matrix. The concept of balances among groups of variables is based on a peculiar real coordinate system designed over binary partitions of the parts of a composition (Egozcue and Pawlowsky-Glahn, 2005). Following an approach similar to that used in the Principal Component Analysis, D-1 balances are searched, so that each one explains a part of the total variance of the geochemical system in decreasing order. In our case the approach was improved by using robust methodologies to calculate mean and variance-covariance structure, thus minimising the impact of outliers on data variability. The developed method was applied to waters sampled in the Mt. Rognosi regional park (Upper Tiber Valley, Central Italy), an area featured by the 1) presence of Jurassic ophiolitic outcrops, 2) CO<sub>2</sub> gas manifestations and 3) cold CO<sub>2</sub>-rich springs (Bicocchi et al., 2013). Results indicate that principal balances are clearly able to distinguish groups of variables with a different spatial stability and continuity, revealing interesting features about the dynamics of the behaviour of the solutes. Moreover, the classical balances approach (Egozcue and Pawlowsky-Glahn, 2005) was also used to propose an alternative diagram to that classically used for water classification (the Langelier-Ludwig square) to visualise both the water chemistry and the relationships among main anions and cations, in the real coordinate system. Finally, a comparison with those plotting the square diagram was carried out in order to look into the behaviour of statistical confidence regions for mean and population data proportions.

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## Assessment of natural background levels coupled with statistical analysis to identify homogeneous hydrochemical areas in a volcanic groundwater body

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Keywords: natural background level (NBL), spatial analysis, Phlaegrean Fields.

Following the Groundwater Daughter Directive 2006/118/EC for the evaluation of the chemical status of groundwater bodies (GWBs) in EU Member States, the determination of the natural background levels (NBLs) in GWBs involves the identification of homogeneous hydrochemical zones. However, GWBs hosted in geologically complex aquifer systems can show relevant differences in groundwater chemistry. The hydrogeochemical features can be affected by peculiar hydrogeological conditions, as reducing conditions, upwelling of hydrothermal fluids, presence of tectonic structures, several degree of interactions with other groundwater bodies and anthropic activities.

In this study, the approach followed to identify homogeneous hydrochemical zones in a volcanic GWB is discussed. A relevant case study was considered: the active volcanic area of Phlegrean Fields (southern Italy), which host a large GWB characterized by the mixing of regional groundwater flow, locally superimposed with a geothermal system and close to the sea. This complex hydrogeological setting is reflected in several hydrogeochemical anomalies, especially the content of arsenic and fluoride.

The NBLs were assessed through the probability plot and the pre-selection methods. Furthermore, geostatistical analysis methods as the Indicator Kriging permitted to obtain probability maps, expressing the probability that, for a given element, at some point, a certain threshold value will be exceeded or not. We considered as threshold values both, the law reference value and the NBLs.

The mapping of the results permitted the distinction between anthropogenic pollution and natural origin of the hydrogeochemical anomalies within the GWB and favoured the delimitation of sectors, where differentiated NBLs should be applied. The high content of As in groundwater results to be of geogenic nature in the southern part of the GWB, where the main tectonic lineaments, the earthquakes and the hydrothermal activities are located, confirming the high potential of the spatial statistical analysis in the groundwater chemical characterisation.

## Multi-scenario groundwater numerical modeling of the Popoli Gorges complex aquifer (Central Italy)

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Keywords: Groundwater, numerical modeling, particle tracking.

Groundwater modeling has become extremely important in the last decades, as it allows to understand groundwater systems, to estimate the parameters of aquifers, to analyze pollution fenomena and to predict the results of certain actions.

In this research, a numerical model has been implemented to test the validity of the hydrogeological conceptual model of the Popoli Gorges complex aquifer, that has been defined in previous studies (Conese et al., 1999; Di Curzio et al., 2014), in order to refine it. For this reason, the groundwater flow, the relationships between groundwater and Pescara river and the transport of polluting particles for three different scenarios have been analyzed.

The Popoli Gorges are the result of the incision of the Morrone limestone aquifer, which has subsequently been filled by heterogenous continental deposits. The porous aquifer is fed by groundwater draining from the limestone aquifer. Moreover, somewhere in the riverbed, the aquifer discharges into Pescara river, highlighting clear groundwater/surface-water relationships.

The numerical model, performed in steady state conditions, has been implemented by means of the computer code MODFLOW-2005 (Harbaugh, 2005). The procedure for defining the numerical model consists of 3 main steps: (1) horizontal and vertical discretization of the numerical domain, (2) assignment of the hydraulic properties to the active cells, and (3) selection of the most appropriate boundary conditions. The model has been calibrated using the "trial and error" method, by means of hydraulic head measurements (summer 2007), and adapting the hydrodynamic parameters. Using the post-processing code ZONEBUDGET, the inflow from the limestone aquifer and the discharges into surface-water have been calculated. In addition, MODPATH (Pollock, 2012) has allowed to obtain the paths of the polluting particles, coming from an important polluted site located in the study area.

Under normal pumping conditions of the wells-field, or when it is turned off, Pescara river drains the aquifer; instead, in case of over-pumping, aquifer is fed by the river. Furthermore, due to the different behaviour in the three scenarios, there is a noticeable difference in the number of particles that are intercepted by the wells.

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#### Impacts of nitrogen depositions on groundwater systems in northern Italy

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Keywords: Atmospheric pollution, nitrogen deposition, vadose zone

In the last decades, a large effort has been carried out to reduce atmospheric pollutant emissions in Europe. Improvement of air quality, reduction of the acidity of atmospheric deposition, and decrease of nitrogen compounds ( $NO_3^-$  and  $NH_4^+$ ) carried to terrestrial and aquatic ecosystems are targets of European directives (2001/81/EC, 2008/50/EC, 2016/2284/EU). However, despite the progresses of the last 30 years (Rogora et al., 2016), water and soil acidification, nutrition unbalance in forest trees, and eutrophication in surface waters are still of great concern.

Nutrients that fall on the ground from the atmosphere represent a minor component of the total N input to soils, especially when compared to agricultural, civil and industrial inputs (EEA, 2005). Although often underestimated, this source apportionment becomes a part of leaching from the soil to groundwater. Therefore, the overarching goal of this study is to identify anthropogenic background values of pollutants in groundwater, not related to direct sources of contamination (e.g., industrial wastes, leakages from sewage systems, fertilizers). Specific objectives are: i) to quantify and characterize pollutants in atmospheric depositions; ii) to evaluate how pollutants infiltrate and redistribute in the unsaturated soil.

Wet deposition is measured at 15 monitoring sites, homogeneously distributed in the western sector of Lombardy Region in northern Italy and characterized by different potential emission sources (i.e., natural areas, agricultural fields, and urban agglomerations). Rainfall collection during each single rainfall event started in February 2017. After collection, samples were analyzed for the major physical and chemical parameters (pH, EC, major anions and cations).

In June 2018, an instrumented field site will be settled to reconstruct the path of nitrogen through: 1) atmospheric emission; 2) wet and dry depositions; 3) infiltration through the ground surface and the vadose zone; 4) addition to groundwater storage. Results from the monitoring campaign at the field site will allow the calibration of a numerical model, which could help in identifying the impacts of atmospheric emissions on groundwater quality in different environmental contexts (e.g., natural, urban and agricultural areas).

Results of the first year of monitoring revealed a dependence of N depositions on local meteorological and emission conditions. The average concentration of nitrate in precipitation during the monitoring period was 5 mg L<sup>-1</sup>, allowing an estimate of the wet deposition of inorganic N (as  $NO_3^{-1}$ ) of 11.5 kg ha<sup>-1</sup> yr<sup>-1</sup> (average annual precipitation in the period 2013-2017 was about 1000 mm). As nitrate leaching from soils generally increases at N deposition rates higher than about 10 kg ha<sup>-1</sup> yr<sup>-1</sup> (Butterbach-Bahl et al., 2011), this work suggests that the N atmospheric input to soils could not be neglected when evaluating the impacts of nitrate sources to groundwater contamination.

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## Geogenic sources of fluoride contamination in groundwaters of Northeastern Ghana: Bongo district in perspective

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Keywords: Fluoride, Groundwater, Geogenic.

Groundwater is the major source of drinking water in most urban and rural communities in Ghana. However, the groundwater in most parts of northern Ghana contain fluoride concentrations exceeding the acceptable limit (1.5 mg/L) postulated by the World Health Organisation (WHO). The situation is unbearable in the Northeastern segment of the country as Bongo district in this area has been severally reported to have elevated fluoride concentrations in the underlying groundwater. However, interpretations on the source of the fluoride is yet enigmatic though recent researches have pointed a geogenic source for the origin of the fluoride (Alfredo et al., 2014; Sunkari et al., 2018). Therefore this study is aimed at confirming the geogenic sources of the fluoride by an integrated fluoride concentration analysis, hierarchical cluster analysis and mineralogical analysis. A total of thirty (30) borehole water samples and ten (10) rock samples proximal to the water sources were collected in various communities in the district during the dry season. The fluoride concentrations vary between 1.71 and 4.0 mg/L, exceeding the permissible limit of the WHO. These values are comparable to those reported in earlier literature. The cluster analysis reveal three spatial groundwater associations; the first cluster comprises groundwaters from communities having fluoride concentrations less than 3.5 mg/L but greater than 2.0 mg/L, the second cluster includes communities with fluoride concentrations in their groundwater generally less than 2.0 mg/L but greater than 1.7 mg/L. However, the third cluster involves communities with groundwater fluoride concentrations less than 4.1 mg/L yet greater than 2.7 mg/L. These variations suggest that the second cluster is the most homogenous since it presents lower fluoride concentrations as juxtaposed to the first and third clusters and its lower limit is only slightly higher than the WHO guideline value of 1.5 mg/L. The analysed rock samples are all biotite-granites collectively known as the "Bongo granite" which display hypidiomorphic granular textures with quartz, microcline, plagioclase, biotite, muscovite and variable amounts of hornblende and amphibole as the main constituents. Out of these, the most abundant fluoride-bearing mineral is biotite (KMg<sub>2</sub>[AlSi<sub>2</sub>O<sub>10</sub>]F<sub>2</sub>), which correlates well with the fluoride concentrations in the analysed water samples sourced from the district. This implies that the elevated fluoride concentrations in the district is due to the high dissolution of biotite in the groundwater and the adequate groundwater-rock interaction, hence confirming the geogenic source of fluoride in the area. Dental fluorosis commonly occurs among indigenes of the district due to the consumption of water contaminated with fluoride.

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#### Groundwater Circulation in Karst Aquifers of the Umbria-Marche Apennines

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Keywords: Karst, Carbonate rocks, Groundwater flow.

The Umbria-Marche Apennine has a large number of karst springs that drain water stored in carbonate formations. The aim of this study is to understand the hydrological mechanisms behind groundwater circulation in this area and their relationship to the structural and stratigraphic settings of specific aquifers.

Recession analysis (Master Recession Curve method) and time series analysis (auto- and cross-correlation functions) were applied to the daily discharge of six karst springs monitored over eight years (from 2007 to 2015). Both analyses indicated the presence of two types of karst aquifers: aquifer with unimodal behavior and aquifer with bimodal behavior. Scirca, Vaccara, Boschetto and Bagnara springs are characterized by two hydrodynamic sub-regimes, in which fracture networks control the baseflow with recession coefficients of about 10-3 day-1 and conduit networks control the quickflow with recession coefficients of one order of magnitude lower. In contrast, San Giovenale and Capo d'Acqua springs present only one hydrodynamic sub-regime related to fracture network drainage, with recession coefficients ranging from 10-3 to 10-2.

Time series analysis confirm the results of recession analysis, showing a large memory effect (over 80 days) and a large response time (over 100 days), implying the dominance of the baseflow sub-regime.

These results indicate that the Maiolica Formation is characterized by a high degree of fracturation and slight karstification, which control infiltration and percolation; whereas the Calcare Massiccio Formation regulates groundwater circulation in the deeper zones of the aquifer, characterized by a high degree of karstification through moderately developed conduit networks.

## Session S34 Monitoring of deformation of structures and ground surface displacements

Conveners AND CHAIRPERSONS Claudia Meisina (Università di Pavia) Luigi Guerriero (Università del Sannio) Diego Di Martire (Università di Napoli Federico II) Giuseppe Centolanza (Dares Technology, Castelldefels, Spain) Chiara Calligaris (Università di Trieste)

# The "Franarisk" project in Rome metropolitan area: a tool for land planning and management and for preliminary risk assessment of infrastructures and buildings

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Keywords: landslide inventory, risk assessment, Rome metropolitan area.

In the frame of its institutional duties, the Provincia di Roma promoted, since 2005, studies on landslide susceptibility as a preliminary step in a broader process, aimed at landslide risk assessment of its territory. Methodology was firstly outlined by collaborating with Roma TRE University and ENEA. The susceptibility analysis is based on the quantification of relations between landslides, inventoried in the institutional database and integrated with further surveys, and a number of predisposing parameters, represented in 1:10,000 scale. With the recent reform of local government in Italy, the former Provincia was abolished and replaced by a new institution, the Città Metropolitana di Roma Capitale (CMRC). By collaborating with "Sapienza" University of Rome- Department of Earth Sciences, CMRC in 2016 performed a homogenization of data and studies to date produced, covering about 1.000 km<sup>2</sup> and representing one fifth of the metropolitan area (Argentieri et al., 2016).

Attending its civil protection responsibilities, CMRC started at the end of 2017 a new project, once again in partnership with the "Sapienza" University, for a complete analysis of landslide susceptibility over its whole territorial jurisdiction (about 5300 km<sup>2</sup>). The project is structured in three consecutive phases, to be completed in 18 months:

- A. Vectorial data collection (lithology; land cover; digital elevation model; road network; hydrography; landslide inventories; infrastructures and relevant buildings); the lack of a complete 1:10.000 scale geological map of the entire metropolitan area, only partially available, induced to choose the Regione Lazio 1:25.000 as reference layer, allowing a homogeneous cover of the study sector.
- B. Landslide susceptibility analysis for each typology (rock fall/topples; roto-translational; slow creep; flowslides), following the Logistic Regression method.
- C. Preliminary risk assessment for buildings, road network and infrastructures, by means of spatial overlay operations, considering both slow and fast mass movements.

The FRANARISK project will provide a useful tool for land planning and management and civil protection, in terms of sustainable development and natural risks prevention in the Rome metropolitan area. Spatial overlay operations will allow preliminary assessment on risk exposition of CMRC properties, particularly focusing on road network and high school buildings.

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### Risk prevision and prevention in Rome metropolitan area: the "IOPS project" for school buildings

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Keywords: school buildings, SMAV method, soil-structure interaction.

In the frame of its institutional duties, the *Città Metropolitana di Roma Capitale (CMRC)* promoted a vulnerability analysis program of its high-school buildings, according national legislation concerning strategic and relevant edifices. Management of such real estate was in fact one of the main responsibilities for the former *Provincia di Roma*, since its foundation; in the recently reformed framework of local government in Italy, it remains to the new Authority.

After the onset of the Central Apennines seismic sequence in August 2016, further activities for risk prevision and prevention on *CMRC* high-school buildings have been started. Although in the Rome metropolitan area edifices and infrastructures are not highly prone to earthquake damage, the main shocks of the sequence (2016, August 24th; October 26th and 30th; 2017, January 18th) were perceived throughout the whole territory, including Rome urban area. After the 2016-10-30 mainshock, preliminary surveys on school buildings were carried by *CMRC* technical staff, revealing in fact no significant evidence of damage. Nevertheless, *CMRC*, attending its civil protection duties, decided to face this issue in a specific program and, at the end of 2017, a cooperation was thus started, including *CMRC*, *Università degli Studi Roma TRE* and *Dipartimento della Protezione Civile*, in order to better understand "far field" effects of earthquakes from Apennines seismogenic zones. Firstly, an application to *CMRC* high-school edifices of the *SMAV* method (Seismic Model from Ambient Vibrations; Acunzo et alii, 2015a,b) was planned. The aim of this experimental project is to evaluate the *IOPS* (Operational Condition Index) for those buildings, supporting the *CMRC* vulnerability assessment program.

A selection among the over 300 existing schools was made, in order to pick-up representative case studies. Consequently, considering both buildings structural characteristics and available geological and geophysical subsoil data of each site, we selected a sample of 15 buildings for experimental measurements; the aim of the study is to evaluate their actual operational condition in different geological frameworks. This first step will guide further studies based on preliminary results.

Moreover, a prior communication campaign, presenting the project and its goals to teachers and students of each involved school, will represent a useful tool for spreading the culture of prevention, improving their state of awareness.

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## Measures of ground deformation obtained using satellite sensors to characterize the aquifer-system properties of the Madrid Aquifer-system (Spain)

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Keywords: ground deformation, Persistent Scatterer Interferometry (PSI), Madrid Aquifer-system (Spain).

The measurements of aquifer-system ground deformation represent an important tool to examine the surface response to groundwater levels variations. However, data scarcity over space and/or time is a major limitation for the aquifer-system deformation monitoring. Even where ground-based monitoring systems (such as Global Positioning System, GPS or extensometers) exist, there is often a lack of long term monitoring data and a limited number of monitoring sites due to their costs.

Persistent Scatterer Interferometry (PSI) is an efficient monitoring tool to measure the spatio-temporal ground displacements over large areas with millimetric accuracy. The aim of this study is to present the application of PSI-based ground deformation measures to characterize the aquifer-system properties of the Madrid Aquifer-system (Spain). Therefore, PSI data acquired by ERS-1/2 and ENVISAT satellites during the periods 1992-2000 and 2002-2010, respectively, has been exploited to calibrate a 3D finite-element groundwater flow and geomechanical model. PSI-based ground deformation measurements have contributed to understand that the aquifer-system behaves almost elastically, experiencing land subsidence and uplift related to extraction and natural recovery cycles driven by the drought periods occurred in summer 1995, 1999, 2002, 2006, and 2009. The results show the effectiveness of an integrated approach composed of PSI-based ground deformation measurements and 3D geomechanical model to support aquifer-system characterization over large areas.

#### Ground deformation related to the old Lungro Salt Mine: a multidisciplinary approach

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Keywords: Lungro salt mine, InSAR, water geochemistry.

Lungro village is located in the northwestern Calabria Region (South Italy) and it is characterized by widespread landslides, known since historical time. Close to San Leonardo area, previous works recorded several tens of centimeters of subsidence by means of a topographic survey carried out between 1999 to 2005. In correspondence of this site, we analyzed Envisat SAR data (see Cianflone et al., 2015) using multi-temporal InSAR technique. We observe subsidence signals with value up to  $\sim$  -6 mm/yr, mean velocity value of  $\sim$  -3 mm/yr and absence of ground displacement close to the Lungro village and in the Carrocchia site respectively. We also considered three ascending displacement time series for the San Leonardo hill spanning from 2003 to 2005, located in the middle and along the two sides respectively. The analysis shows surface movements between -10 and 20 mm for the central sector, and -5 and 5 mm along the two sides according to the topographic data. At the San Leonardo foothill, is located the old Lungro salt mine (active since Magna Grecia epoch), consisting of a mine with a total length of 400 m along 5 levels, at depth varying from -90 m to -240 m, where Messinian halite deposits were mined.

In order to evaluate the possible relation between the observed ground displacements and the dissolution of the evaporitic successions, a geochemical survey and mineralogical characterization are carried out.

Salt dissolution is highlighted by the salinity up to 3000 mS/cm measured in the river and springs water collected close to the salt mine. For each sample several in field groundwater parameters are measured (pH, Eh etc) and concentrations of major and trace constituents by HPLC and a quadrupole ICP-MS. Geochemical study allowed to identify one main geochemical water type: NaCl (Cl ~ 500 ppm) linked to an interaction with halite.

The future goal is to well understand the relation between ground deformation and halite dissolution. The latter is detailed investigating also by mineralogical characterization (SEM/EDS and Optical Microscopy) of the halite crystals. Preliminary analysis shows that halite crystals do not have cubic habit but elongated shapes with evidence of dissolution on the grains boundary, all main primary structures (including the Fluid Inclusions) are obliterated.

Our preliminary study has shown a link between the surface deformation and the still active halite dissolution in the old salt mine. For this reason, to better investigate the active deformation of the area, we suggest a monitoring system including both ground displacements time series (by means of ground-based and remote sensing techniques) and observations of the halite dissolution evolution through continuous stream water and groundwater analysis.

Cianflone, G., Tolomei, C., Brunori, C.A. & Dominici, R. (2015): InSAR time series analysis of natural and anthropogenic coastal plain subsidence: the case of Sibari (Southern Italy). Remote Sensing, 7, 16004-16023.

## Mud volcano in Santa Barbara village (Caltanissetta, Sicily) - an "open air" morphometry laboratory. Relationship between vertical deformations and evolution of the hydrographic network

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Keywords: morphometry, mud volcano, hydrographic network.

A mud volcano located in central Sicily (Caltanissetta) was used as an analogue to understand active tectonic phenomena at a regional scale.

This site provides the ideal conditions for quantitative morphology studies. It was possible to quantify the variations of the hydrographic network in a very short transient phases. The rapid vertical movement of the surface induced by the activity of the mud volcano, the lithological uniformity (only argillaceous deposit) and the small size of this structure represent the best conditions for applying morphometric analysis.

An accurate surface model of the mud volcano was obtained by aerophotogrammetric surveys using the "Structure for Motion" (SfM) technique. The products of this method are: high resolution DEMs (average cell size 0,017 m) and orthophotos.

These products were developed on the GIS platform, where the basins and hydrographic networks of the structure were carried out. The morphometric parameters (linear, areal and landform properties) of the various basins have been calculated by specific software.

The comparison between the data acquired since October 2016 highlighted the variations in the landscape forms from a quantitative view.

In general, we can state that all the morphometric parameters, compared to the theoretical values, respond faithfully to the transient phases immediately subsequent to deflection and inflection of the sedimentary volcanic complex.

The hydrographic network evolution caused by mud volcano vertical deformation can be compared to the regional morphometric variations due to active tectonic processes.

#### **GIS-based interpolation methods for spatial assessment of Geogenic Radon Potential**

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Keywords: Soil gas radon, spatial regression, Geogenic Radon Potential.

Modelling the spatial variability of Geogenic Radon Potential (GRP), based on spatially continuous geological, geographical and geochemical information as proxy data, is an important task to identify radonprone areas and provide the local administration of a useful tool for land use planning and strategies aimed at radon health risk reduction (Ciotoli et al., 2017). In this work, different interpolation techniques in a geographical information system (GIS) environment are applied and compared for estimating the spatial variation of GRP in the municipality of Celleno and Caprarola (Viterbo, Lazio, central Italy). The research activity has been conducted within the European LIFE-Respire project.

Two spatial regression models such as Geographically Weighted Regression (GWR) and Empirical Bayesian Regression Kriging (EBRK) were applied to investigate the relationships between soil-gas radon concentrations and some proxy explanatory variables, and to generate the GRP map of the studied areas. Geographically Weighted Regression is an extension of the traditional OLS regression, but it assumes that the relationships among the independent variables are not constant over space, then GWR calculates local regression coefficients and local r-squared values (R<sup>2</sup>) rather than global coefficients. Empirical Bayesian Regression Kriging is very recent implementation of the spatial regression modelling; it is a geostatistical interpolation method that uses Empirical Bayesian Kriging (EBK) with raster explanatory variables that are known to affect the value of the data of the response variable to interpolate. This approach combines kriging with regression analysis to make predictions that are more accurate than either regression or kriging techniques. Regression models and semivariograms are estimated locally with simulations; and explanatory variables are transformed into principle components prior to modelling to solve multicollinearity problems.

The regression models have been performed using the following proxy (i.e., explanatory) variables: the natural content of the radiogenic elements (Ra, U, Th, and K), the emanation coefficient of the outcropping rocks, the diffusive <sup>222</sup>Rn flux from the soil, the soil-gas CO<sub>2</sub> concentration, the Digital Terrain Model (DTM) and Topographic Position Index (TPI, a DTM-derived morphometric parameter), the permeability of the outcropping rocks (derived from the map of the hydrological complexes) and the gamma dose radiation of the shallow lithology. Soil-gas radon measurements were used as the response (i.e., dependent) variable of the applied regression models. Data has been organised in two subsets (training and test data) to be used in the validation process. Results from validation technique indicate that GWR provides a local model with a better performance than the global OLS model. However, the application of the EBRK will result in the best model validation vs the validation of the GWR result.

Research was conducted and funded within two research projects: INAIL/CNR-IGAG (P19L06) and LIFE-Respire (LIFE16 ENV/IT/000553).

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#### Remapping of hydrogeological risk areas in regional planning: execution of direct and indirect geognostic surveys, monitoring and updating of maps - Locality of Ceramica -Iglesias - SW Sardinia - Italy

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Keywords: Remapping, Geological Risk.

As part of the research into the design of the Public Works Area of the Province of Southern Sardinia, it was necessary to intervene to carry out important projects in-depth detailed studies near an area subject to collapses and active gravitational movements (sinkholes). The area, located in the locality of Ceramica in the Municipality of Iglesias, is used as a multifunctional sports center with a high concentration of daily users, is located near a cluster of production sites, for which there are several studies that have identified a system of Cenozoic faults that have moved the calcareous paleozoic base (Formation of and the subsequent tertiary soils of sedimentary nature of the Formation of the Upper Eocene Cixerri - Oligocene). The structuring of the area, known in the literature as a "structural bass" oriented in the E - W direction, identifying the homonymous graben delimited by faults of similar orientation, has recently had a possible new reading as a syncline of growth within a zone between two fault-reversing fault-oriented NW.

The execution of direct surveys to continuous coring was carried out on five locations 30 - 40 meters apart, up to a depth of 40 meters. At the same time, seismic and geoelectrical investigations were carried out in order to map the entire study area in detail. Through the stratigraphic data obtained it was possible to reconstruct the succession in situ in detail, thus being able to obtain an accurate structural geological model, such as to be able to calculate the main tectonic movements occurred in the tertiary stratigraphy encountered in the drilling performed. The relative rejection (over twenty meters) and the displacements to which the investigated lands were subjected have been oriented and correlated with each other, thus identifying a fault, still part of the tertiary system that characterizes the Fossa del Cixerri, not yet identified from previous surveys carried out on the area.

The structural reconstruction given by the study of the cores, supported by the geophysical surveys performed on the alignments identified by the probing points, led to the execution of electrical and seismic prospecting (superficial and in hole) configured in such a way as to bring a data restitution tomographic.

The overall study of the area, carried out for building purposes, within the planning of public works of the Province of Southern Sardinia, could thus give support to the area's management knowledge, verifying and implementing the previous knowledge of the area of intervention, with a contribution of data accompanying the previously known stratigraphy, with a cartographic remapping following the execution of the studies of greater detail, which led to a substantial reduction of the risk parameters.

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# An innovative approach to study complex landslides through InfraRed Thermography and DInSAR

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Keywords: Infrared Thermography, DInSAR, Landslide monitoring.

Complex landslides are usually characterized by numerous features controlling their evolution and making their modeling a hard procedure. A direct approach to the study of a landslide, through field surveys and geognostic campaigns, is the starting point for a reliable modeling. Nevertheless, this is not always entirely feasible, especially when landslides cover wide or impervious areas. Therefore, remote sensing methodologies represent a supporting tool to characterize peculiar features of the mass movement, to monitor its evolution and to detect specific elements which cannot be easily identified by the human eye, such as slow motions or peculiar ground conditions. In this study, the combination of InfraRed Thermography (IRT) and Differential Interferometry SAR (DInSAR) applied to the remote surveys of landslides is presented with the purpose of testing their coupled attitude in this field. The first one recently proved a valuable tool to identify specific elements along slopes (e.g. bare areas, vegetated sectors, presence of water, lithological variation), and to map jointed and weathered portions of rock masses (e.g. Mineo et al., 2015). It is based on the detection of the thermal radiation emitted by all forms of matter in nature, which is mostly invisible to the naked eye. The analysis of thermal images allows highlighting interesting contrasts, which can be related to specific conditions of the investigated landslide. DInSAR analyzes long data sets from satellite images, detecting displacement measures with high accuracy, thus representing a reliable tool for the long-term monitoring (e.g. Confuorto et al., 2017). The above described techniques were employed to survey landslides occurring in northeastern Sicily, along the Nebrodi Mountains, and showing worrying signals of potential reactivation. IRT allowed recognizing ancient landslide bodies and slope portions characterized by incipient movement, as well as peculiar geological contacts. At the same time, DInSAR confirmed the active state of some movements and their potential evolutive trend, in terms of direction of motion and velocity, especially in correspondence of critical spots identified by IRT. Achieved results demonstrate the reliability of the combination of IRT and DInSAR to survey mass movements and provide an innovative scientific approach that can be adapted to similar studies worldwide.

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#### Sentinel-1 InSAR data for semi-automatic detection of coseismic ruptures: the 2016 Central Italy earthquake sequence case study

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Keywords: Interferometry, Sentinel, Earthquake.

A significant sequence of normal-faulting earthquakes occurred in the central Apennines in Italy from August to October 2016 On August 24th, a Mw 6.2 earthquake struck the area close to the towns of Accumoli and Amatrice. Several ground ruptures with decimetric offset along SW dipping extensional faults occurred for over 10 km. Two months later, on 26 October, another mainshock with Mw 5.9 occurred 25 km to the north, near the town of Visso. On 30 October, the largest shock of the sequence (Mw 6.5) occurred in the area between the epicenters of the previous earthquakes. These events reactivated many of the existing ground ruptures and produced further NW-SE trending fractures. We investigated the surface earthquake effects by means of SAR interferometry using Sentinel-1 SAR acquisitions. For the InSAR data processing we used the open source SNAP toolbox. We processed four pairs of acquisitions covering the pre and post seismic period of each main shock. Phase unwrapping was successfully performed using SHAPHU. The unwrapped interferograms were imported in a GIS environment and processed with an InSAR motion resolver tool. This raster calculation tool allows to combine ascending and descending acquisitions very quickly. A slope gradient map has been created using vertical motion values to detect the possible coseismic ruptures. Rupture traces are inferred from the displacement gradient maps considering steps with a slope higher than 40 degrees. The InSAR outcomes relative to the Amatrice event highlight quite accurately the well field documented displacement of the Mt. Vettore western flank. Here the geological effect of the earthquake is more than 5 km of ground ruptures. The same rupture system reactivated during the Norcia major event together with a complex surface faulting pattern composed by subparallel and overlapping synthetic and antithetic fault splays. The slope gradient map clearly highlights the continuous NW-SE alignment of ruptures along the Mt. Vettore western flank and partially, in small segments, those in the northernmost sectors. We can clearly identify the rupture at the foot of Mt. Vettore, in the plain, responsible of a road's break. Other possible ruptures, corresponding with known tectonic features, are also identified. Results match quite well the field data. From a methodological perspective, this approach allows to obtain a quickly preliminary map of the possible ground ruptures. Moreover, it demonstrates the effectiveness of the Sentinel-1 data for this purpose. The methodology could allow to detect the fractures evolution during a seismic sequence. Also, it can be useful as a field guide to speed up the detailed survey, especially in large or remote areas. In this case study, the best identified surface ruptures are those with throws greater than 10 cm. Improved results could be achieved using a high resolution DTM for topographic phase removal and defining good strategies for filtering and classify results.

#### Low-cost MEMS accelerometers for tilt measurement: thermal compensation and accuracy assessment

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Keywords: MEMS accelerometer, thermal drifting, inclinometer.

Low-cost MEMS accelerometers have a wide range of application in consumer electronics and are being increasingly used for geotechnical applications like infrastructures and landslides monitoring (De Capua et al. 2013; Huang et al., 2013; Li et al., 2014). Despite their advantages over traditional electromechanical sensor like smaller size and power consumption, and the existence of controlling platforms, such as Arduino®, that make these and other sensors suitable for low cost monitoring application (e.g. Guerriero et al., 2017), MEMS accelerometers have the disadvantage to be very sensible to temperature variation. Such sensitivity induces thermal drift that need to be corrected before to use them for monitoring purposes.

On this basis, and as a first step toward the development of a real-time continuous landslide monitoring system, we analysed the thermal behaviour of a low-cost MEMS accelerometer and compensated its drifting in a temperature range of -10 to +45 °C. To simulate MEMS behaviour during positive and negative temperature variation, we developed a miniaturized and tiltable thermal chamber. We made multiple rising and falling measuring cycles. Each measuring cycle was completed at a specific inclination of the sensor. For our analysis we used steps of 5 degree of inclination in a range  $\pm 45^{\circ}$  for both the X and Y axes.

This procedure provided 37 residuals vs temperature curves. Acquired data were used to reconstruct a surface of compensation for each axis. Such surfaces were interpolated in Matlab®. Derived polynomial equations were used for thermal compensation of MEMS. Before the compensation, the RMSEs were of 284 and 161 LSB for the X and Y axes, respectively. After compensation the RMSEs were 11 LSB for X axis and 8 LSB for Y axis. Raw data were used to calculate the X and Y angles and associated RMSEs. Before compensation, we estimate RSMEs of 1 degrees for the X axis and 0.57 degrees for the Y axis. After compensation, such RMSEs decreased to 0.039 and 0.026 degrees, respectively.

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#### A case study of flash flood magnitude evaluation in Southern Apennines

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Keywords: Flash Flood, Alluvial fan.

Flash flood events may reactivate torrential streams that feed alluvial fans and represent a common natural hazard in Southern Apennines, where at their foothills several towns are present. Sometimes, these events are assumed as flow-like landslides, even if they are different in terms of rainfall, triggering conditions, solid concentration, flow velocity and heights, volumes and consequently the damages.

In this study, the methodological approach followed for the assessment of the magnitude in a torrentialflooding event is proposed. In particular, magnitude is meant as the mapping and analysis of both erosion and deposition area, particles sizes distribution, water heights measurements and finally damage assessment.

The event of the 14th-15th October 2015 in Solopaca - Paupisi area (Benevento) is adopted as an interesting case study, which was surveyed by both classical and modern technologies, as UAV images. The surveyed parameters were collected in a DB and summarized into thematic maps. The area of the event and the thickness of the deposits permitted to estimate the magnitude of the event in terms of solid transported volume.

The collected data and their elaborations provided useful information, which can be adopted to calibrate physical-based models aimed at simulating future scenario in watersheds characterized by similar geologic and geomorphologic setting.

#### Monitoring slope deformations in the complex Senerchia earthflow by traditional and UAV surveys

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Keywords: UAV, Earthflow, Monitoring.

The complex Senerchia earthflow is located in the upper Sele river valley, (Campania, South Italy). It affected the varicoloured clays flysch by an extension of nearly 2 km and has mobilized more than 1 million m<sup>3</sup> of material. The earthflow exerienced several reactivation phases, after 1980 Irpinia earthquake, in 90s, in 2014 and it is actually active. The event is characterized by a retrogressive movement of the head scarp, which affected some regional roads and it is threatning Senerchia town itself.

After the recent-most reactivation, a novel investigation campaign was carried out, it consisted of six stratigraphic boreholes, where 8 undisturbed soil samples were collected for the laboratory testing. Each borehole was equipped for displacements measurement through inclinometers, together with four piezometers with continous groundwater table data recording.

The geological and geomorphological surveys coupled with seismic and geolectric surveys permitted to identify the sliding surface, located at 15 m depth and to update the landslide geological model and its relationships with groundwater flow. The monitoring of both displacements and groundwater table was carried out on a four years period.

In the upper part of the landslide, where the retrogressive evolution is occurring, four UAV surveys for a total length of 1 km were carried out. The obtained 50 cm resolution DEMs permitted through the DoD (Dem of Differences) to highlight morphological variations in terms of depletion and accumulation areas, while the displacements of the GPS targets in both the stable and moving areas permitted to measure velocity and displacement vectors of the landslide body. The most relevant deformations attained a value of 40 m in only 2 months of observation, in the central part, which is deforming faster than the flanks, favoured by prolonged rainfalls occurred in the 2017 - 2018 hydrologic year.

The landslide of Senerchia is a relevant case study for testing novel monitoring techniques through drones survey, which can also provide useful information on the kinematics of large landslides in rapid evolution.

#### Risk mitigation plan for transportation civil infrastructures in Rome Metropolitan Area

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Keywords: bridges, civil protection, load carrying capacity.

Transportation civil infrastructures provide in Rome Metropolitan Area the range of essential services necessary to support quality of life and the economy. Management of road network mas in fact one of the main responsibilities of the former *Provincia di Roma*, since its foundation; in the recently reformed context of local government in Italy, such duty remained to the new Authority, the *Città Metropolitana di Roma Capitale (CMRC)*, which in 2015 replaced the former *Provincia*.

The ability to move goods, people and information safely and reliably is nowadays of increasing importance for the CMRC, in order to guarantee infrastructure operation in spite of natural and anthropic hazards. After the recent collapse events in Italy, that caused serious damage and in some case victims, it became urgent the need for a quick though effective tool for the analysis of the performance of the infrastructural properties. For this purpose, on December 2017 it was established a collaboration project between CMRC and Università degli Studi Roma TRE, aimed at the definition of a method to be developed through different steps. A large amount of information on the CMRC infrastructures was firstly collected so as to carry out quantitative and qualitative analyses; to this purpose, we could rely on the databases and archives of the CMRC (STEPA). At the same time, specific aspects of the local transport network were analyzed, in order to define network priority criteria and basic indices for their evaluation (STEP B). Subsequently, all types of structures were classified and analyzed in order to define a set of specimen structures, e.g. bridges (STEP C). Specific inspections and investigations on the selected set of structures were planned (STEP D). Finally, the ultimate purpose of the proposed method is to provide tools for the evaluation of load carrying capacity for the existing bridges (STEP E), supporting *CMRC* in the management of its structures and improving their operational safety level. Moreover, an overlay of the transportation structures position with mapping of landslide and flooding hazard has been performed, in order to evaluate infrastructures that are more critical and address further detailed investigations for civil protection purposes.

#### Present-day surface uplift of the European Alps: mechanisms, relative contributions and implications for hazards

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Keywords: Alps, present-day uplift, modeled contributions.

Understanding how the Earth's topography evolves in space and time is central to the Earth Sciences, and assumes particular relevance in orogenic contexts. The elevation, relief and overall geomorphology of mountain ranges are dictated by intrinsic (i.e. isostatic) and extrinsic (i.e. dynamic) forces, which evolve accordingly to the tectonic and climatic history. Discerning between the primary tectonic or climatic origins of measurable time-variations in mountain elevation allows quantifying the dominant forces at play, but detailed constraints on the many interdependent processes and topographic effects involved by tectonic and climatic changes are required.

The most updated measurements of surface vertical displacements of the European Alps show widespread rock uplift at rates of up to  $\sim 2.5$  mm/a in the north-western and central Alps and  $\sim 1$  mm/a across a continuous region from the eastern to the south-western Alps. Such uplift rate pattern is at odds with the horizontal strain rate field, characterized by shortening and crustal thickening in the eastern Alps and very limited deformation in the central and western Alps. Proposed climate- or tectonic-controlled mechanisms of uplift include lithospheric adjustment to the deglaciation, erosion and/or detachment of the western Alpine slab, as well as lithospheric and surface deflection due to the sub-Alpine asthenospheric flow. However, integrative quantifications of these contributions to match the currently observed surface vertical motion of the Alpine topography are lacking. Here, I critically resume previous quantifications and present new estimates of the contributions from all potential mechanisms. The lithospheric adjustment to deglaciation and erosion accounts for the majority of the observed surface uplift rate budget in the eastern Alps, which suggests that topographic growth by horizontal shortening and crustal thickening is hampered by subsidence due to the eastern Alpine slab pull or lateral escape of crustal material. In the central and western Alps, the lithospheric adjustment to deglaciation and erosion accounts for roughly half of the uplift rate budget, which points to a noticeable contribution by possible mantle-related processes such as detachment of the European slab and/or asthenospheric upwelling. Although to date it is difficult to constrain even the first order pattern and magnitude of mantle-controlled contributions to ongoing Alpine vertical displacements, future AlpArray-related data shall provide additional insights. In any case, cooperative tectonics- and climatic-controlled processes, rather than an individual forcing, best explain current measurements of Alpine uplift. This regional investigation should be used as a priori information for any basin- or Alpine-scale risk management plans involved with the geomorphological adjustment to active deformation processes by, for instance, landslide morphodynamics.

## Multidisciplinary investigations to characterize a shallow fault zone in the Bellolampo landfill (Palermo, Italy)

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Keywords: Fault zone, ERT, SRT.

An integrated analysis approach, based on geological investigations and 2D high-resolution shallow geophysical data, was proposed along a slope in the Bellolampo landfill area (Palermo, Italy) where the presence of a fault zone was hypothesized. The surveys were supported by a detailed photogrammetric survey.

Geological surveys, carried out in correspondence of over 60 measurement stations, provided hundreds of stratigraphic, sedimentological and mesostructural data in order to define the kinematics of the main tectonic elements.

Moreover, several integrated geophysical surveys have also been performed using electrical resistivity tomography (ERT), induced polarization tomography (IPT) and seismic refraction tomography (SRT) techniques. Coincident topographic traces were used for the electrical tomographies, in order to facilitate the joint interpretation of the different geophysical methods and to apply a cluster analysis approach. These techniques have shown excellent results when applied to seismic and electrical tomography data (Gallardo & Meju 2003; Bohm et al. 2017; Capizzi et al. 2017).

In the study area, two trenches (perpendicular to the direction of the fault being studied and parallel to it, NW-SE and NE-SW respectively) have been realized to analyse the fracturing pattern and the stratigraphic features. Along the excavation walls, a NE-SW directed zone composed of intensely deformed carbonate breccias in an yellowish-dolomitic matrix crops-out. This zone has been correlated to a continuous band recognized in depth, for all the crossed thickness, with variable lateral characteristics, in the geophysical sections acquired in the area. This zone corresponds to a Mesozoic extensional fault zone affecting the Mesozoic carbonate platform succession.

Based on the collected and processed data, the geological model of the site was defined. The integrated geological and geophysical analysis and the k-means cluster analysis allowed to reconstruct the lateral variations of the deformed carbonate breccias and better define the stress-field-orientations. The fracturing and kinematic analysis on fault planes observed along the trenches, highlighted systems of left and right-lateral transtensional faults NW-SE, NNW-SSE and NE-SW trending, respectively, which antedate the extensional tectonic event.

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Gallardo, L.A. & Meju, M.A. (2003): Characterization of heterogeneous near-surface materials by joint 2D inversion of dc resistivity and seismic data. Geophys. Res. Lett. <u>http://dx.doi.org/10.1029/2003AL017370</u>.

## Session S35

## **Fast-moving landslides:**

## criteria and methodologies of hazard zonation and monitoring

Conveners AND CHAIRPERSONS Domenico Calcaterra (Università di Napoli-Federico II) Giovanni Battista Crosta (Università di Milano-Bicocca) Francesco Maria Guadagno (Università del Sannio) Giovanna Pappalardo (Università di Catania) Micol Rossini (Università di Milano-Bicocca)

#### Evaluation of triggering factors and thresholds of large landslides in alpine environment

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Keywords: Landslides, Triggering, Threshold.

Rainfall, snowfall, snow melting and infiltration are parameters that influence the large landslide occurrence in mountain areas. The evaluation of the relationship among these parameters drives the possibility to estimate the landslide trigger thresholds. In Piemonte region, during last decades, several landslides have been monitored by ARPA Piemonte using manual and automatic inclinometers, GPS, piezometers and others geotechnical monitoring instruments, that has been compared with information provided from the meteorological network (temperatures, rains, snow cover and snow depth) and with field surveys and stratigraphic analysis. This study deals with the Borgata landslide in the Sestriere Municipalities (Piedmont, Italy). It is a very slow rock-debris slide with and estimated area of about 200'000 m<sup>2</sup>, included into a slope affected by a Deep seated Gravitational Slope Deformation (DSGSD). The main sliding surface is at about 12-15 m of depth. The landslide causes recurrent damages to the main road and, in case of paroxysmal evolution can involve the Borgata Township. Field surveys, stratigraphic analysis and monitoring data are available since 2002, with a constant dataset available.

During the last 5 years, the Borgata landslide underwent four main accelerations during the springtime, detected by inclinometric measures and confirmed by field evidences. In order to estimate the prevailing parameter among the above mentioned ones we perform the "Moving sum" method on the last 5 years dataset. In detail we analyzed the 3, 7, 15, 30, 60, 90, 120 before each monitoring day series of data of precipitation, temperature, snow cover and infiltration showing several exceedings of the values recorded in correspondence with the landslide activations.

Because of this, a new infiltration index derived from FEST-WB model (Flash - flood Event - based Spatiallydistributed rainfall - runoff Transformation - including Water Balance) (Ravazzani et al., 2010) was used to flank the traditional variables, showing a sensible relationship between calculated FEST-WB index infiltration and paroxysmal phase of every single movement. Based on the movement occurrences, fixing infiltration thresholds at 17 mm and 28 mm respectively in the 3 and 7 days prior to the event (evaluated as triggering factor) and 66 mm, 103 mm and 121 mm in 15, 30 and 60 days before (evaluated as predisposing factor), we limit at few cases the false positive values. The result of this preliminary study is that the infiltration index derived from FEST-WB model can be considerate with a good confidence a reliable parameter to indicate landslide activation and as alert indicator.

Ravazzani, G., Rabuffetti, D., Corbari, C., Ceppi, A. & Mancini, M. (2010): Testing FEST-WB, a continuous distributed model for operational quantitative discharge forecast in the upper Po river. Proceedings of the AMHY-FRIEND International Workshop on Hydrological Extremes, Cosenza (Italy), July 10-12, 2008.

#### Landslide inventory and rockfall risk assessment of the Monte Pellegrino Oriented Nature Reserve area (Sicily)

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Keywords: Landslide inventory, Rockfall risk assessment, Strategic urban areas.

In the last 20 years the natural oriented reserve of Monte Pellegrino is affected by several rockfall events. This sector of the Northern Sicily is a strategic urban area and represent the most important element of both the religious and cultural tradition and landscape for the city of Palermo. The rockfalls are here the major natural threats and represent a relevant risk of people, structures and infrastructures and prevents the economic and social development that could be made by high tourist potential of the area. For the above mentioned reasons a detailed geological and geotechnical study in order to define a quantitative risk analysis is now being carried out, concurrently with the implementation of the landslide inventory essential for analysis and monitoring. Monte Pellegrino, located along the Alpine orogenic belt (Catalano et al., 2013) in the emerged Sicilian fold and thrust belt, is an isolated carbonate massif characterized by the presence of poor rock masses and steeply sloping hillsides. The quantitative risk analysis was performed through several steps and taking into account the provisions of directive which is in force in the local institutions. The spread of a rockfall depends on many control factors such as geological setting and geomechanical features for both source area and below area, it is therefore necessary to define different input elements: an inventory of landslides, a database of factors and a dataset that contains the results of the on-site inspections like the geostructural and geomorphological data. The archive of landslides occurred over a period of 20 years was created; the spatial database (constructed in accordance with the standards) contains information on the identification code and date of the event, location, type, involved lithology and related thematic maps. Other thematic maps are those requirements deriving from the factors layers as tectonic features, morphological characteristics, geometric attributes of the slope, type of coverage, structures and infrastructures, trajectory of the block and the stop point. The above mentioned steps allow the implementation and calibration of the model for rockfall analysis; in particular, by means backanalysis stage it is possible to determine the restitution and friction coefficients through a comparison of the points where the rock blocks stop in the simulation with the rockfall history stop points. The next step we took is to produce the map of those areas with different degree of risk defined through the density of the trajectories reconstructed through the model. Finally, are presented here two between the cases studied needed to set up the forecasting model for the rockfall trajectories.

Catalano, R., Valenti, V., Albanese, C., Accaino, F., Sulli, A., Tinivella, U., Gasparro Morticelli, M., Zanolla, C. & Giustiniani, M. (2013): Sicily fold-thrust belt and slab roll-back: the SI.RI.PRO. seismic crustal transect. Journal of the Geological Society, 170, 451-464.

# Preliminary stability assessment of the rocky cliffs of the archaeological site of Crapolla (Amalfi coast, Southern Italy) through UAV photogrammetry

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Keywords: Landslide, hazard, rocky cliff.

Crapolla cove is a suggestive, from a landscape, natural and archaeological point of view, inlet of the Amalfi coast, in the Massa Lubrense municipality (Napoli province, Southern Italy). It is, indeed, not only valuable for its geographical position and wonderful setting, but also for conserving ancient traces of a past full of history. Almost at the bottom of a 700-steps path, the St. Peter chapel can be found, recently built on the rests of a Benedictine abbey, dating back to the 10<sup>th</sup> century A.D., where columns and marble bases and other rests are visible. Crapolla is located in the southern part of Massa Lubrense municipality, just in front of three islets, Li Galli, Isca and Vetara. From a geological point of view, the presence of limestone rocks is predominant. In detail, the main outcropping formation is the *Calcari a Radiolitidi*, Lower Cretaceous in age, formed in a carbonate platform environment. A pebble beach at the bottom of the cove has been shaped by the stream final delivery. The most prominent morphological elements of the cove are represented by two rocky cliffs, made up of carbonate rocks, higher than 100 m and with evident signs of fracturing and erosion, both of gravitational and karst nature. As to correctly assess the stability of the two rocky cliffs, a photogrammetric survey campaign by means of Unmanned Aerial Vehicle (UAV) has been performed, also taking into account the impervious and therefore difficult to access setting. Through such tool and trough following post-processing operations, two orthophotos of both the cliffs, characterized by frontal view, have been obtained. Such products provided an optimum base for a correct assessment of the stability scenario of the Crapolla cove: on one hand, a geo-lithological map was produced as to distinguish different lithologies, according to their lithological and geological homogeneity, and to recognize the main discontinuities which may imply a higher failure predisposition; on the other hand, a geo-morphological map was realized to identify the main morphological elements, ascertaining also the properties which could result significant to the cliff instability. The geo-lithological and the geomorphological maps were thus used to produce a susceptibility map based upon a combined litho-geomorphological approach, by subdividing the study areas in homogeneous units, as a function of the engineering-geological expected behavior and classifying them according to the priority of intervention. Quantitative analysis and data extraction were also performed in a preliminary way, by using the orthophotos, to identify and define the potential failure mechanisms of the rocky cliffs. In such way, a complete analysis of the risk scenario has been obtained, providing useful indications to design the most suitable mitigation works in view of a future and safe tourist access to the Crapolla area.

#### Slow ground instability in the Caltanissetta industrial area related to mud volcanism: insight from an integrated approach

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Keywords: Mud Volcanism, Photogrammetry, Well Logs.

The industrial area of "Calderaro" is located in southern part of urban area of Caltanissetta, one of the most densely populated cities in central Sicily, affected since 1970 by slow ground instability. This process caused serious damages to industrial buildings and infrastructure networks, determining a high geo-hazard scenario. Only 1 km far the damaged industrial area is located an active mud volcanoes zone named Santa Barbara Maccalube, affected in last decade by paroxysmal activity, consisting in alternating ground deformation and violent mud eruption. The entire investigated zone is geologically located in the Caltanissetta Basin, a Late Miocene to Quaternary dynamic foredeep basin placed between the southern part of the Maghrebian-Apennine Chain and the northwestern margin of the Hyblean Foreland. The Neogene-Quaternary sediments filling the top thrusts basins of the central Sicilian belt are characterised by the occurrence of several lenticular bodies of mud breccia. These bodies, made of a brecciated to cataclastic clayey matrix containing exotic blocks, represent the result of mud diapirism occurring along the frontal part of the central Sicilian accretionary wedge. On the base of a multidisciplinary investigation, characterised by integrated geomorphological and geological surveys, boreholes logs, geotechnical data, geophysical investigation and Advanced Differential Interferometric SAR data analysis, we suggest a direct correlation between the sedimentary volcanism and morphological instability of the study area.

## The geological monitoring of a rock wall and the activity for the safety and protection of human life and of cultural heritage

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Keywords: geological monitoring network, rock wall, civil protection.

The Gallivaggio rock wall, in the San Giacomo Filippo district (Sondrio province), has been monitored by ARPA Lombardy's Geological Monitoring Centre (CMG) since 2011 because the area has had periodic single rock block falls. In this area there are the main mountain passage ("SS route 36"), a restaurant, some houses and the important heritage site ("Sanctuary of Gallivaggio "built at the beginning of 17 century).

ARPA CMG has carried out a variety of observational approaches on- site to manage the geological monitoring in Gallivaggio during the last few years; specifically (2011) The planning and installation of the first geological network with the MEMS accelerometer and strain gauges, from which periodic measurements are taken by involving ground SAR (Synthetic Aperture Radar) radar, (2014) the first years of data analysis acquired by geological monitoring followed by appropriate modification and adjustment of the network, (2015) modelling assessment began and trigger identification with the establishing of suitable movement thresholds, (2016) activation of near real time monitoring with ground SAR radar, (May 2017) conclusion of modelling study and information transferal to Civil Protection, municipality and prefecture.

The first years of monitoring and study permitted a categorization of two main conditions. The first, a more frequent but less hazardous one which is the single block fall. This is impossible to predict and has a 2-22% possibility of overriding the iron nets. The second one is the fall of 5-6000 cubic meters of bedrock (Truzzo granite) present at the top of the rock wall and marked by a large fracture.

During the Autumn of 2017 the data analysis values acquired, enabled us to notify the Lombardy Region Civil Protection of a dangerous acceleration of movement in the rock area regarding the second scenario. After a few months (18th February) we sent another notification in which we informed the Civil Protection about the acceleration that evolved doubling of values with respect to ones from in Autumn.

Thanks to this observation, Civil Protection and Mountain Community began work to stabilize the rock volume of 5.000 mc and the Civil Protection advised the Mayor of San Giacomo Filippo to evacuate the area of the Sanctuary until the end of the undertaking. Then, on 13th April from the identified area single rock blocks began to come down and hit the road and Sanctuary. During the days following the houses and restaurant were also evacuated and the road was closed for 18 hours a day.

In conclusion, it is possible to verify that a suitable monitoring network plan and strategy realised by a reliable remote monitoring system, allowed us to alert the Civil Protection and the Municipality during a worsening of landslide movements and demonstrates the utility of an organized management of a monitoring geological network, as in the one which exists in Lombardy Region, for the safety and protection of residents and of cultural heritage.

#### Satellite-based monitoring of ground deformations in the city of Cuenca (Ecuador)

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Keywords: DiNSAR, landslides, monitoring.

Ground deformation phenomena, intended as earthquakes, landslides, subsidence and sinkholes, have a notoriously significant destructive power and are a primary cause of economic and social losses. Aiming at the prevention and planning of risk reduction measurements, the monitoring of such events is highly recommended. In this sense, both in the scientific community and among the land management authorities, the application of Remote Sensing techniques is considered a relevant and useful innovation, able to provide rapid information on wide areas and with relatively low costs. Among these techniques, Differential Synthetic Aperture Radar Interferometry (DInSAR) has shown its great potential for the monitoring of a wide range of ground deformation phenomena, improving its performances thanks to the launch of the most recent and accurate constellations (e.g.: TerraSAR-X, COSMO-SkyMed) and the development of several DInSAR approaches (e.g. PSInSAR, SBAS, SqueeSAR<sup>®</sup>, RMT, etc.). In this work, the whole territory of the city of Cuenca (Ecuador) has been monitored through the use and the processing of COSMO-SkyMed imagery (acquired in the time-span 2015-2018). The city of Cuenca, the third of Ecuador for number of inhabitants, has grown on three fluvial terraces within the Sierra (a part of the Andes chain) at a height of 2.500 m a.s.l. Due to the geographical and geological setting, Cuenca has repeatedly suffered from landslides, especially along the external sectors of the city, placed along the piedmont of the surrounding slopes. Here, a SAR data post-processing procedure has been adopted, the so-called LaDIS (Landslide Detection Integrated System), also used in the framework of the third Not-Ordinary Plan of Environmental Remote Sensing in Italy (Di Martire et al., 2017), to identify anomalous areas, i.e. those aggregates or clusters of PSs which, for physical and spatial characteristics, might testify to instability. Such procedure is extremely useful when dealing with very high density of targets, where is not easy to detect real movements of the ground. A significant number of anomalous areas was detected and, it is worth to mention the active sectors in correspondence of the University of Azuay, in the southern area, where displacement rates of 30 mm/yr have been detected. Therefore, the use of DInSAR methods and of postprocessing procedures confirms the efficacy of remote sensing data to detect landslides and define their state of activity. Such aspect may represent a very valuable contribution to a correct land management and emergency planning in highly populated cities such as Cuenca.

Di Martire, D., Paci, M. Confuorto, P., Costabile, S., Guastaferro, F., Verta, A. & Calcaterra D. (2017): A nation-wide system for landslide mapping and risk management in Italy: The second Not-ordinary Plan of Environmental Remote Sensing. International Journal of Applied Earth Observation and Geoinformation, 63, 143-157.

# Insights into clay-landslide movement propagation and slide-to-flow transition from sediment discharge calculation and field observations, Mount Pizzuto, southern Italy

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Keywords: landslide, movement propagation, slide-to-flow.

We studied the short-term behavior of the Mount Pizzuto landslide in southern Italy in order to understand its kinematics, movement propagation and slide to flow transition during surging events. This landslide affects the northeastern side of the Pizzuto Mount and involves an estimated volume of 300,000 m<sup>3</sup> of fine-grained clavrich flyschoid material (Guerriero et al., 2016, 2017). Its movement is highly seasonal with major acceleration/ reactivation concentrated in the spring (e.g. Guerriero et al., 2015). The Mount Pizzuto landslide has several kinematic zones, with transitional areas marked by changing structural styles, from compressional structures (thrusts) upslope to extensional structures (normal faults) downslope. For our analysis, we used displacement data from multiple GPS surveys of a network of benchmarks and the reconstructed 3D geometry of the landslide to compute sediment discharge at kinematic-zones transition sections. These data were interpreted on the basis of field observations. The results suggest that during surge events, flow acceleration starts within the head and propagates downslope inducing a cascade effect between kinematic zones. During surge, the average sediment discharge is nearly constant, and a change from sliding to flowing allows propagation of movement towards the toe. During slow movement, kinematic zones are independent and sediment discharge varies along the flow. In general, the velocity profile and the structural style are controlled by the basal slip surface. The implications are: i) sediment discharge is not constant but is a function of the landslide activity, ii) during surge, clay-rich material behaves similar to an incompressible fluid, and iii) the distribution of surface structures can provide information about the geometry of the slip surface and the velocity profile. Additionally, clay landslide with a well-defined neck seem to be more likely to surge with respect to those without.

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Guerriero, L., Revellino, P., Luongo, A., Focareta, M., Grelle, G. & Guadagno, F.M. (2016): The Mount Pizzuto earth flow: deformational pattern and recent thrusting evolution. Journal of Maps 12, 1187-1194.

Guerriero, L., Diodato, N., Fiorillo, F., Revellino, P., Grelle, G. & Guadagno, F.M. (2015): Reconstruction of long-term earth-flow activity using a hydro-climatological model. Natural Hazard 77, 1-15.

#### Qualitative and quantitative approaches to estimate rockfall hazard and risk

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#### Rockfall, Risk assessment, Event Tree.

Rockfalls are fast and unpredictable landslides, caused by the detachment of a rock boulder from a slope, with a fast evolution in space. Due to their high destructive power, they are among the most studied geomorphic processes, especially in mountainous areas, where structures and infrastructures represent common elements at risk. Risk arising from rockfalls is the probability that an uncertain, sudden, and extreme hazardous event can cause damages to one or more exposed elements. Therefore, its assessment is an essential procedure in the perspective of mitigation works and territorial zonation. Several methods for hazard and risk assessment are available in literature, and their degree of complexity varies with respect to the final purpose of the computation. Qualitative methodologies allow a quick estimation of the hazard or risk based on field data and technical assumptions, while quantitative approaches involve more complex models of, among others, geology, geomechanics, slope stability. In this study, two cases are presented with reference to (1) the quantitative risk assessment along a strategic linear infrastructure in a mountainous contest and to (2) the qualitative hazard assessment for a preliminary zonation of the Taormina carbonate cliff (northeastern Sicily). In the first case, geological and geomechanical surveys are coupled with the purpose of achieving a full knowledge of the main criticalities of the area, repeatedly affected by numerous rockfalls (Pappalardo et al., 2014; Mineo et al., 2017). Rockfall simulations were performed and a probabilistic model through the Event Tree Analysis approach was developed to assess the probability related to the bad consequences arising from potential rockfalls. In the second case, a hazard zonation through the Evolving Rockfall Hazard Assessment procedure (ERHA) was carried out at the Taormina cliff (Mineo et al., 2018). Outcrops underwent a geomechanical characterization through field surveys and kinematic analyses, which allowed ascertaining the predisposition of to failures through specific kinematic patterns. Moreover, rockfall trajectory simulations were performed to estimate the intensity of potential events. Results of both procedures allowed the production of thematic maps showing the spatial distribution of hazard and risk and their interaction with the main elements at risk.

Mineo, S., Pappalardo, G., Mangiameli, M., Campolo, S., Mussumeci, G. (2018): Rockfall Analysis for Preliminary Hazard Assessment of the Cliff of Taormina Saracen Castle (Sicily). Sustainability 10 (2): 417.

Mineo, S., Pappalardo, G., D'Urso, A., Calcaterra, D. (2017): Event tree analysis for rockfall risk assessment along a strategic mountainous transportation route. Environmental Earth Sciences 76:620.

Pappalardo, G., Mineo, S. & Rapisarda, F. (2014): Rockfall hazard assessment along a road on the Peloritani Mountains (northeastern Sicily, Italy). Nat. Hazards Earth Syst. Sci., 14, 2735-2748.

#### Relict landslide detection at the cultural heritage site of Abakainon necropolis (NE Sicily)

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Keywords: Relict landslide, Abakainon necropolis, Cultural Heritage.

The Greek colony of Abakainon was a founded in northeastern Sicily by Sicels, in a strategic location from the military and trading points of view. Recent archaeological excavation campaigns allowed discovering a buried city, with precious and well-preserved finds, and a wide necropolis area with about 150 well-preserved tombs, dated between the end of the fourth century BC and the beginning of the second century BC. Several tombs are partially collapsed or broken, probably due to a natural event. From a morphological point of view, the necropolis lies on the flank of a NNE-SSW trending steep slope, on a portion characterized by a slightly flatter morphology, which reminds an old landslide body. Starting from this element, new geomorphological and geophysical investigations were carried out with the purpose of looking for evidence of landslides and tectonic structures close to the necropolis area and of finding out if the necropolis was really built on a landslide body. Geomorphological surveys highlighted crucial aspects on the interaction between tectonics (mainly fault segments) and main geomorphological features (e.g., river path, crest lines, landslides), as several deviations of crest lines and river path, as well as plano-altimetric ruptures, which were surveyed at the intersection with tectonic structures. Geophysical surveys, mainly aimed at passive ambient noise measurements, allowed recognizing three main characteristic impedance contrasts, which were correlated with peculiar elements of the study area such as (1) a deep geological contact between the crystalline basement and the overlapping sedimentary cover, (2) the old landslide sliding surface, (3) buried tombs (Pappalardo et al., 2018). Moreover, strong directional effects at some recorded H/V spectra highlight the occurrence of fault segments bordering and even affecting the landslide body. This is a key evidence, proving that the necropolis was built on a relict landslide, which occurred before the latest reactivation of the surveyed faults. In this perspective, it is likely that Abakainon necropolis collapsed because of the shaking of an old earthquake, whose action was probably enhanced by a site effect caused by the presence of the relict landslide body on which the necropolis itself was built. This can explain the current setting of tombs and ruins at the necropolis site. Achieved results confirm that the presented multidisciplinary approach is a suitable tool to clarify the geology of an area, especially where faults and landslides are not easy to survey due to local restriction of a heritage site.

Pappalardo, G., Imposa, S., Barbano, M.S., Grassi, S., Mineo, S. (2018): Study of landslides at the archaeological site of Abakainon necropolis (NE Sicily) by geomorphological and geophysical investigations. Landslides DOI 10.1007/ s10346-018-0951-y.

#### The potential of deterministic and probabilistic physically based approaches on the prediction of rainfall-induced shallow landslide: an application from slope to catchment scale in the city of Rome

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Keywords: Shallow landslide, Back analysis, Rome.

Rainfall-induced shallow landslides are one of the most frequent and widespread natural hazards all over the world. This type of landslides is triggered during intense and/or prolonged rainfalls involving topsoil covers in either colluvial or eluvial nature. The analysis of such phenomena is still a challenging task because of the numerous parameters accounted into the triggering mechanisms. In particular, the numerous slope failures, typically occurring also in constrained areas, and their instantaneous initiation make difficult the spatial and temporal forecasting of their occurrence in order to support a sustainable land use management and geohazard mitigation policies.

The city of Rome (Italy) has particularly been affected by this specific hazard over the years. The most recent event occurred in 2014 during which nearly 70 slopes failed all around the city, thereby causing important damages on the human-built assets. In respect of this and preceding landslide events, numerous data have been collected (inventory maps, rainfall recordings...); however, there is still a consistent lack of further analyses related to landslide risk on this important Italian city such as high resolution zonation studies.

In this work, physically based models have been performed for the back-analysis of the major landslide event occurred from the 31st January to the 2nd of February 2014. On those days, an exceptional rainfall event occurred with a maximum of 46 mm/hr. Intensive field surveys have been carried out and laboratory analyses performed on the soil samples outcropping over a representative area of the city i.e. Monte Mario hill (0.75 km<sup>2</sup>). Data from these technical investigations have been used to perform a deterministic evaluation of the slope stability scenarios through the calculation of safety factor (FoS) with TRIGRS (Transient Rainfall Infiltration and Grid-based Regional Slope Stability) model. Extending the study area, variances caused by complex inherent intrinsic hydro-geotechnical properties soil samples have led to a great variability of data. In respect to this, the probabilistic version of the above-mentioned model has therefore been implemented to evaluate the slope stability condition during that particular critical rainfall period within a larger area in the city of Rome (99 km<sup>2</sup>). In this area, no specific point data and dense surveys are available, hence the assessment of the slope stability conditions are expressed in terms of the probabilities of slope failures related to FoS. More specifically, we compared the results from the two different approaches with the real landslide source areas mapped after the event. This work has also highlighted the importance of the vegetation on the slope stability by performing trials of cohesion values in order to set the lower bounds at the initial condition where no cell was found unstable.

#### Remotely-sensed optical indicators of vegetation dynamics for landslide monitoring

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Keywords: landslide monitoring, remote sensing of vegetation, sentinel 2.

Landslides are a widespread hazard in the Alps and monitoring them is crucial for risk management in this region. This study aims at developing a novel approach for slow-moving landslide monitoring based on the identification of remote sensing indicators of landslide activity linked to vegetation dynamics. In particular, our study is based on the hypothesis that the vegetation on the landslide body is expected to experience different conditions, compared to that on an undisturbed control area, such as alterations in biomass production and variations in the phenological cycle (e.g. senescence anticipation). The approach has been tested on 12 landslides in Lombardy region and, once fully validated, will be applied on a bigger landslide database consisting of c.a. 5000 slides. We used the newly available ESA Sentinel-2 images, characterized by an unprecedented combination of high temporal, spatial and spectral resolution, to generate temporal series of vegetation indices (e.g. NDVI, NDII) over the year 2017. The temporal series extracted from vegetation inside and outside the landslide bodies showed different vegetation dynamics captured by the temporal trend of the vegetation indices tested, showing the suitability of remote sensing indicators linked to vegetation dynamics to monitor landslide activity.

#### Insights on the role of initial soil conditions in shallow landslide triggering: a physically-based approach from laboratory to slope scale

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Keywords: shallow landslides, flume tests, physically-based model.

Shallow landslides are instability phenomena that typically occur in response to intense and/or prolonged rainfall events, affecting superficial deposits of reduced thickness (1-2 m) such as colluvial and debris covers. Considering the characteristics of this type of landslides (i.e. high velocity and energy impact, absence of warning signs in field), such events represents a serious threat for human activities: for this reason, in the last years numerous methods have been developed for the evaluation of their spatio-temporal occurrence. Many of these methods are based on physically-based models that try to extend over large areas simplified slope stability analyses using physical and mechanical parameters of the involved material. However, the parameterization of such models is usually challenging even at the slope scale, due to the numerous parameters involved in the failure mechanism. In particular, considering the scale of the phenomenon, the role of transient hydrology is essential. From this point of view, the above-mentioned models generally incorporate this component assuming a slope-parallel flow either in its steady state as a function of slope and drainage area (steady-state models) or by dynamically evaluating the entire process from rainfall to the transient response of the groundwater (dynamic models). However, in both cases the effect of initial soil conditions (in terms of porosity and soil moisture) cannot be disregarded.

For this reason, in this work we analyze the triggering mechanisms of shallow landslides evaluating the effect of the initial soil conditions through laboratory flume experiments. Specifically, numerous tests have been performed on a soil sampled on Monte Mario hill (Rome). This area has been affected by recurring rainfall-induced landslide events in the past, including the one that occurred between 31<sup>st</sup> of January and the 2<sup>nd</sup> of February 2014. In this sense, the outcome of the experiments has been also analyzed in relation with the results provided by TRIGRS (Baum et al., 2008), a physically based model that predicts the timing and spatial distribution of rainfall-induced landslides over large areas. Specifically, the insights resulting from the laboratory tests have been used to better define the constraints of the physically-based model for the back-analysis of the 2014 landslide event.

Baum, R.L., Savage, W.Z. & Godt, J.W. (2008): TRIGRS - A Fortran program for transient rainfall infiltration and gridbased regional slope-stability analysis, version 2.0. U.S. Geological Survey. Open-File Report 2008-1159, 75 pp.

# X-ray microtomographic investigation for the engineering-geological characterization of landslide-prone pyroclastic deposits in the peri-Vesuvian area (Campania region, Italy)

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Keywords: Landslide, modelling, pumice.

Campania region has been severely hit by catastrophic events such as landslides in the last decades. In particular, in the hills surrounding Mt. Somma-Vesuvius, characterized by pyroclastic deposits mantling the carbonate bedrock, the massive landsliding episode of Sarno and Quindici, occurred on May 5, 1998, is reminded as the most tragic one, counting 160 casualties. Pyroclastic deposits cover large part of the Campania region, with major thickness in proximity of the most recent and important volcanic center, the Somma-Vesuvius complex. The assessment of the geological and geotechnical parameters of the terrains is of crucial importance for modelling the triggering factors of such kind of events, being the peri-Vesuvian geological and stratigraphical setting very prone to landsliding. To this last aim, both field measurements and laboratory analyses on representative samples might contribute to an exhaustive model of the engineering-geological conditions of the terrains. Laboratory analyses may be carried out through conventional techniques as well as through innovative microanalytical methodologies, aiming at the definition of the permeability of pyroclastic deposits and their hydraulic conditions. The test area selected for this study is the Palma Campania territory (Napoli province), located to the east of the volcano and at the footslope of a steep Apennine hill. Palma Campania territory is characterized by pyroclastic deposits of Vesuvian origin covering the Late Cretaceous carbonate bedrock. In such setting, a landslide event occurred in 1986, which killed 8 people living in two houses located at the immediate footslope. In detail, the studied volcanoclastic sequence is constituted by white and grey pumice and dense black scoriae levels, referred to the "Pomici di Base" Vesuvian eruption (22 ka). Representative samples were collected in 13 stratigraphic sections along the slopes of Vallone Lupici at Palma Campania, at various stratigraphic levels, and analyzed to define their structural and textural features. Hence, grain-size analyses were carried out along with specific gravity measurement, coupled to X-ray microtomography, which allowed to define 3D textural properties. The preliminary values of porosity, density and permeability related to the pyroclastic samples suggested a more accurate investigation on the vertical variations of pumice layers physical properties, both at macro- and micro-scale, and an improved evaluation about their influence on landslide triggering factors.

## **Session S36**

# The urban landscape: geomorphological historical evolution, geomorphosites and high risk scenarios

Conveners AND CHAIRPERSONS Maurizio Del Monte (Sapienza, Università di Roma) Pierluigi Brandolini (Università di Genova) Laura Melelli (Università di Perugia) Valeria Panizza (Università di Sassari)

#### Geomorphological map of the urban area of Palermo (Italy)

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Keywords: Urban landscape, Geomorphological mapping, Human activities.

The results of a geomorphological survey carried out in the urban area of Palermo are described. The study area is located in the northern margin of Western Sicily and is part of the SE-verging Alpine orogenic belt (Catalano et al., 2013). An E-W mountain range (Sicilian Apennines) is the topographical expression of this belt (Di Maggio et al., 2017). In the Palermo area, the physical continuity of the mountain range is broken by a large topographically-depressed coastal area. This area is set on a half-graben and is characterized by a plain (Conca d'Oro plain), opened to sea and surrounded by wide scarps hundreds of meters tall to the inland. The wide and tall scarps are abandoned coastal cliffs derived from original fault scarps. Large talus slopes bound the scarps at their base. A very slight dipping wedge of Calabrian coastal and shallow water clastic deposits from few to tens of meters thick crops out in the Conca d'Oro plain. These deposits (Marsala synthem, ISPRA 2013) lie on Meso-Cenozoic rocks with strong angular unconformities. Along the plain, a Middle-Upper Pleistocene succession of marine terraces develops from 0 m up to 150 m a.s.l. These terraces are characterized by large and well-preserved polycyclic wave-cut surfaces which in turn are down-cut by some river valleys from few to ten meters deep. The city of Palermo rises along the marine terrace surfaces and the river valleys of the Conca d'Oro plain. Over the last 2700 years, the urban area of Palermo has been affected by remarkable man-made changes to the topographic surface and to the drainage network. The main changes consist of: filling of river valleys; concreting, diversion and burial of riverbeds; excavation of aqueduct tunnel (*qanat*) and underground or open quarries; massive nourishment of the coast areas by means of demolition materials of the Second World War. Geomorphological setting, man-made changes, and urban development up to the talus slope expose the city of Palermo a hydraulic, sinkhole, and landslide risks. To facilitate study on urban planning and environmental risk assessment, a geomorphological map of the urban area of Palermo has been achieved through field surveys, multitemporal analysis of aerial photographs and topographic map, consultation of historical documents, and stratigraphic and topographic reconstructions from numerous wells.

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#### Mapping Geoheritage on the Official Italian Geomorphological Maps: a Proposal From the Italian Scientific Community

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Keywords: Geomorphological maps, geoheritage, geosites.

At an international level there is currently a great variety of geomorphological legends which differ one from the others in their content, adopted symbols and scale of representation, since a single, universally recognized legend has not vet been implemented. Similarly, there are also numerous examples, at an international level, of thematic maps concerning geomorphosites, especially directed to a public of non-specialists. Recently the Italian Association of Physical Geography and Geomorphology (AIGeo) is undergoing the revision of the official Italian geomorphological legend at different scales. Within this framework, the AIGeo Working Group "Geomorphosites and Landscape" is dealing with the proposal for the inclusion of geomorphosites in the official geomorphological maps at 1:50000 scale covering the entire Italian territory. The AIGeo Working Group on Geomorphosites puts in evidence the importance of indicating, on the official geomorphological maps and, in particular, on documents used for territorial planning, those landforms assessed as geomorphosites. The innovation introduced with this methodological proposal just concerns mapping geomorphosites in the official geomorphological documents and the novel method for their representation. Being the process of surveying and assessment of these landforms more exposed to subjectivity, the criteria followed by operators for geomorphosites selection must be made clear and reported in proper illustrative notes associated to the official geomorphological maps. The effectiveness of the methodology is going to be tested by means of cartographic essays by several researchers of the Working Group, coming from different Italian Universities (Milano, Trieste, Modena, Genova, Urbino, Roma, Napoli, Cagliari, Sassari). The essays cover most of the morphogenetic and morphoclimatic contexts of the Italian territory, mirroring its significant geodiversity. The purpose is to verify and validate the methodology facing the complexity of many different typologies of landforms and highlighting its strengths and weaknesses in order to improve it.

#### Geosites and geological landscape map of Liguria (Italy)

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Keywords: Geosite, Geological Heritage, Ligurian landscape.

Since the beginning of the Third Millennium, an ever-increasing interest of geoheritage has been observed, either in scientific terms or in practical point of view, with the resulting socio-economic consequences.

Geoheritage represents the basic element of the landscape and it often has strong links with other elements of the territory like historical geography, land-use setting, landscape protection, nature conservation, etc. Oneimportant link is tied to the environmental protection task, because most part of the Italian protected areas are mainly established above Earth Sciences features. Consequently, a lot of geosite sare included into these important natural sites.

The issue of geoheritage and geosites has become object of national and regional laws: in Italy the cultural heritage and landscape code was issued in 2004 while in Liguria the Regional Law n. 39/2009 establishes the rules for the valorisation of the geodiversity, geosites and karst areas.

Here we present an overview of geosites and geological landscape of Liguria (North West Italy); in addition to the recent regional database and georeferencing activities of the Ligurian geosites, through a reworking of a simplified geological map addressed also for non-geologists, a geotematic map has been defined. In particular, this product emphasizes the relationship between geology and landscape, showing how different rock masses produce several landforms of outstanding natural beauty in the ligurian territory.

The map shows the basic concepts of geoscience by looking closely at the landscape we see in front of us every day. From the coast to the Alps and Apennines watershed, we identified several geological landscape units characterized by specific rock masses, soils and particular geological and geomorphological features, such as: 1) Palaeolandslides landscape; 2) Ligurian alluvial floodplains; 3)Ligurian coastal plains; 4) the Flysch rock masses; 5) Ophiolitic crags; 6) Conglomerate peaks; 7) Karstic massif; 8) Quartzite and Cherts rock masses; 9) Sandstone spurs; 10) Shales and schists domain; 11) Windows on the Paleozoic; 12) Plio-Quaternary landscape.

More than 500 geosites classified in a recent specific regional database were then overlapped on the geological landscape units: they have been distinguished according to interest, for different geothematic categories, according to the proposal of enhancement.

The Ligurian geosites and geological landscape overview map could represents a friendly tool to identify the most relevant regional geological heritage.

#### Geological and morphological features of the landscape of Catania (eastern Sicily)

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Keywords: paleo-topography, geological model, urban landscape.

The area of Catania shows some spectacular characteristics that have firstly attracted the Calcidesi settlers in 728 B.C. The peculiarities of this site derived from the combined effects of the active collision deformation, the regional uplift and the Etnean volcanism. The active deformation produced a wide ENE-WSW oriented ramp anticline, elongated beneath the urban area. The regional uplift governed the marine terracing and river entrenching, along the coastal slope from Catania to Acicastello. The marine terraces and the river incisions carved a monotonous marly clay sedimentary substratum, undercutting the earlier etnean volcanics (140-132 ka). Recent Lava flows (< 15 ka) form an almost continuous thin cover on the very varied Late Quaternary paleo-topography.

In the northern part of the modern city and in the adjacent outskirts, the volcanic layers conceal the staircase geometry of the terraced coastal slope. In this case, the lava cover contributed to stabilize the entire coastal slope, which is otherwise affected by evident slope instability, due to the high topographic gradient, where the sedimentary substratum is exposed.

In the southwestern part of town, including the old town and the site of the earlier settlements, deeply incised valleys channelized most of the etnean lava flows, causing frequent lateral variations of the volcanic overburden. The volcanic cover is very thin or absent on top of the ancient divides, whereas it reaches several tens of meters within the valleys. In this case, the buried valley acts as the final natural collectors of the ground water supplied by the entire southeastern flank of Mt. Etna. In the old town, the volcanics infilling the paleo-valleys are concealed by the deposits of the 60 ka old marine terrace (OIS 3.3) that is now displaced at about 30 m a.s.l. This raised platform was selected as the earlier site of the town, as it combines a flat elevated topography modeled on loose terrains, ideal for settlement and defense, with abundant groundwater availability. Several springs are located at the mouth of the buried valley, in the eastern part of the town, characterized by a roughly flat, 20 m thick volcanic cover. It consists of large horizontal pahoehoe lava banks that completely conceal the wide buried Holocene marine platform.

The active geological processes severely impacted the evolution of the urban area. The historical lava invasions caused several modifications in the topography of the town (e.g. 1669). The repeated large earthquakes that struck the city produced large amounts of ruins and archeological materials that added to the natural slope deposits contouring the main terrace hosting the old town. As a consequence, large portions of the old town were built, after the A.D. 1693 earthquake, on thick detritus bodies potentially responsible for amplifications of the effects of the future earthquakes.

#### Geological memory sites in the Latium region: a new pilot project

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Keywords: history of geology, geological heritage, geosites.

The aim of this contribution is to share the start, in May 2018, of a two-years pilot project that involves ISPRA, the Regione Lazio and the Città Metropolitana di Roma Capitale.

The purpose of this Collaboration Agreement is to census, characterize and describe the cultural and historical significance of places that we've called "geological memory sites", in the territory of the Latium region.

The geological peculiarity of these sites are closely linked to events or specificities in the heritage, history and culture of the place; values and historical significance of them could be exist only because people or groups of people share in those values.

Most of geological memory sites are characterized by intangible values derived from scientists' feelings about, understanding of, and relationship to the place, its history, its culture, and the uses to which it has been traditionally put.

The identification of the sites will start from the information collected by the History of Geosciences section of the Italian Geological Society; from those produced by the Geological Survey of Italy-ISPRA working group aimed at the retrieval of the geological-historical heritage of the Institute (Cartographical collection, Archive and Library); from the ISPRA National Inventory of Geosites (ING) datasheets. The latter, which can be consulted on the ISPRA website (<u>http://sgi.isprambiente.it/geositiweb</u>), collects reports of geosites throughout the country. The Inventory refers to a geological site of which the geologist recognizes the importance to reconstruct the geological evolution of the territory in which it is located. It has scientific interest, sometimes even landscape, such that is identifiable an interest for its conservation. Within the project introduced here, the scientific interest for the site may, however, not necessarily be the primary one. In fact, we intend to study those places that are first of all characterized by a historical and cultural interest that is related to the geology of the places where human events take place.

We use the term geological memory site, to illustrate the close relation between the place that represents values and traditions, culture and history of the human path and the place as a result of geological phenomena that represent the history of the Earth's evolution.

Starting from geological events (e.g. earthquakes, landslides, etc.) and characters involved in the event (scientists or literates), mining activity, paleontological discoveries, paleoanthropological, paleoethnological and archeological, field trips, the sites identified will be described through datasheets, with text and images, according to a previously defined editorial scheme.

The datasheets will be transferred to a compatible database with ING ISPRA Inventory, and some of the sites identified and described will then be able to become part of the ING.

Upon completion of the project, the datasheets of the geological memory sites will be collected in a thematic volume of the series "Memorie Descrittive della Carta Geologica d'Italia" set up according to the editorial rules of the series.

The researchers involved in the project derive from different scientific education; the working group is composed by: D. Mancinella, D. Mantero, M. Testardi (Regione Lazio); F. Console, S. Falcetti, M.C. Giovagnoli, M. Pantaloni, A. Patanè, M. Vatovec, R. Ventura (ISPRA); A. Argentieri, M. Fabiani, M. Piro, G. Rotella (Città Metropolitana di Roma Capitale), S. Fabbi (CNR), F.M. Petti (MUSE).

#### The gem-quality tourmaline occurring in the Adamello Park natural reservation, Central Southern Alps, Italy

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Keywords: gem-tourmaline, pegmatites, Adamello Park.

An exceptional discovery of gem-quality multi coloured tournalines hosted in Litium-Cesium-Tantalum (LCT) pegmatites, has been made in the Adamello nature park (Adamello Massif, Italy), in the early 2000s.

The area of the finding (Adamé valley) is included within the limits of a special natural reservation of the Adamello Park, where minerals collecting is forbidden. Therefore, in consideration of the scientific importance of this discovery, a joint project to benefit both the scientific and collectible aspects of these tournalines, was organized by the Museum of Natural History of Milan and the regional natural Park (Pezzotta and Guastoni, 2002).

Gem quality tourmalines were never found before in the Alps and this new pegmatitic deposit is of particular interest for the better understanding of the petrological and geochemical evolution of the Adamello tonalitic intrusion and its hosting rocks. Recent literature pointed out how tourmaline, in view of the large numbers of interchangeable elements in its crystal structure, is exceptionally sensible to chemical and physical changings during crystallization, allowing detailed petrologic investigations about the formation environment.

Field investigations showed the presence of polychrome tournaline crystals occurring in pegmatite dikes hosted in the hornfels derived by the contact metamorphism between the Adamello tonalite and the Mesozoic sedimentary sequence. In order to study the original conditions of formation and the paragenesis, accurate sampling and survey of such pegmatites were performed.

The Natural History Museum in collaboration with the National Research Council and the Department of Earth Sciences of the University of Milan, started a series of mineralogical, petrological and gemmological investigations of the collected material.

The preliminary results on a suite of gem-quality faceted tournaline and raw material are presented here. Classical gemmological studies have been performed on faceted stones (0.77-1.22 ct) of green to brown colour. Electron microprobe analyses combined with *laser ablation*-inductively coupled plasma-mass analyses allowed the determination of the contents of the major, minor and trace elements, showing the occurrence of mainly elbaite compositions, with lesser amounts of rossmanite, foitite and fluor-liddicoatite.

This work is included in the Adamello Park activities related to the management of geoheritage and focused on the protection and conservation of minerals. An exhibit of part of the recovered material is now open to the public at the Casa-Museo of the natural Park in Cevo (BS). The remaining mineral and rock specimens are preserved in the collections of the Natural History Museum of Milan.

Pezzotta, F. & Guastoni, A. (2002): Adamello: la pegmatite miarolitica LCT della valle Adamé (Brescia). Rivista Mineralogica Italiana, 3, 127-142.

#### Genoa 'the Superba' old city - Unesco World site - geomorphological heritage

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Keywords: Urban Geomorphology, Geomorphosites, Geotourist itinerary.

The coastal city of Genoa is an increasingly popular tourist destination due to its landscape and cultural aspects. Between 1099 and 1815, Genoa was a maritime republic with naval power and it is today the largest harbour in Italy and the second in the Mediterranean. There are, however, some less known aspects of Genoa cultural heritage connected to urban geomorphology and geo-diversity; in addition to the existing landscape and artistic values, these could constitute another element of interest for tourists and residents. Due to historical and recent urban sprawl, the former morphology of Genoa (the 'Superba') which contributed to the city military and economic success, is today largely invisible. The stratification of urban sprawl phases characterises many ancient cities in the Mediterranean: despite centuries of human intervention, however, the original features of the territory can still be recognized in present-day landscapes.

This study shows the results of long-standing geomorphological surveys carried out in Genoa which allowed a detailed reconstruction of the geomorphological setting of the historical centre, a Unesco World Heritage site since 2006 In addition, this investigation allowed us to identify some sites of geological-environmental and geomorphological interest which are worth of being conserved and promoted for tourism. In particular, we identified three thematic urban trails on the hydro-geomorphological evolution of Genoa historical centre and the environmental-geological settings which conditioned the development of the city: the 'vertical Genoa trail', on the funicular Zecca-Righi and along the old 'creuze', in order to underline the slopes' verticality; the 'Waterways trail', along the final stretch of the old aqueduct and many historical fountains; the 'Genoa zero trail', which develops from east to west across the old centre, looking for traces of the city's old morphology under the current urban cover.

These three trails show how history, urbanisation and geomorphological features of the area are strictly connected. Their promotion for tourism purposes aims to facilitate the understanding and divulgation of what we know about Genoa's geomorphology, alongside with other important features of interests such as the coastal landscape and the cultural and historical heritage.

#### Urban geomorphology of Genoa old city (Italy)

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#### Urban landscape, Geomorphological mapping, Man-made landforms.

A multi-year geomorphological surveys of the city of Genoa allowed the creation of an original geomorphological map of the urban environment. The city of Genoa is internationally known for the importance of its port and for the presence of a historic city center recognized as an UNESCO World Heritage since 2006.

The research methodology was based on the structuring and analysis of a multi-source geodatabase consisting of information acquired from scientific literature and technical reports, historical and recent photographs and maps, geological and environmental data related to land planning plans, original data from field surveys. Work phases of data elaboration included: 1) a multi-temporal cartographic comparison from the eighteenth-century to year 2016; 2) an analysis of aerial photographs in the period 1936-2016; 3) the interpretation of boreholes data; 4) both surface and underground geomorphological observations within the city centre, by means of field surveys and speleological techniques.

The recognition of the former geomorphological setting on which the historical nucleus of Genoa has developed, and the interpretation of its paleogeographic, geological and tectonic conditions, are not an easy task: since the High Middle Ages of the Maritime Republic of Genoa, the superposition of multiple phases of urban sprawl has obliterated original geomorphic conditions. However, interpretation of the rich geodatabase allowed to classify landforms, processes and surficial deposits with respect to their original environment and morphogenesis, i.e due to: running waters, gravity, karst, action of the sea; but, above all, due to human activities. In fact, the entire study area has undergone continuous modifications by man through the all considered time interval, as shown by artificial land fillings at the seaside, alteration of the river network, excavations and fills on the slopes, with the highlighting of significant anthropogenic urban landforms.

The geomorphological map support both a morpho-evolutionary and a functional approach to the geomorphological landscape the of Genoa old city: therefore, it can be a useful tool for land planning, also aimed at reducing the geo-hydrological risk that characterizes the urban area.

#### Interplay between topography and geomorphology with prehistoric settlements: the case study of Ustica island

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Keywords: Ustica island, Geomorphology, Prehistoric settlements.

The island of Ustica is located in the Southern Tyrrenian Sea, about 60 km north of Palermo. The island was intensely inhabited during the prehistory. Archaeologists documented the presence of humans at Ustica since the Neolithic Age (8 ka BP), then in the Eneolithic Age (6 - 5 ka BP), Early Bronze Age (4 ka BP) and Middle Bronze Age (3,4 - 3,2 ka BP). From a geological point of view, the island is the top of a submarine volcanic relief built during the Pleistocene.

This study aims at highlighting the interplay between the local geomorphological features and the choice and development of suitable Prehistoric archaeological sites at Ustica.

The first Neolithic Age settlement was built at the Pirozza hill, on the southwestern sector of Spalmatore. It is a small promontory facing the sea, about 50 m asl, cut on columnar basalts. From the sea, it appears like a fortress. Some archaeologists, on the basis of ceramic pottery, suggest that Neolithic Age populations landed at Ustica from Sicily. The top of Pirozza is part of the MIS5.5 marine terrace (about 125 kyrs BP). The Neolithic Age settlement used this landform in order to dominate the south-western sector and to control the sea between Sicily and the island. The settlement lasted for many years, since there are many archaeological evidences in the surroundings of the site, such as the ceramic pottery at the "Villaggio turistico di Punta Spalmatore".

At Contrada Piano dei Cardoni, in the southern hinterland, there is an Eneolithic Age settlement. Here, at 100 m asl and 500 m landward, many products of the lithic industry have been found, together with abundant obsidian fragments. These remains testify the glass business from Lipari and Pantelleria islands. Here, bedrock is cut on basalt flows of Monte Guardia dei Turchi (520 kyrs BP) covered by a Crotonian marine terrace deposits (350 ka BP). The geomorphological features of the area, sloping toward the sea without natural obstacles, testify the reduced natural defence from the sea. The improved security of the Eneolithic Age pushed the inhabitants to favour the landward sectors, that are more protected by salt weathering and are prone to agricultural uses and sheep-farming.

During the Early Bronze Age, the population returned to extremely defenced sites. The site referred to this period is located on a small relief called Culunnella. From a geological point of view it is a crater located at the Monte Guardia dei Turchi, in the middle of the island, at an altitude of about 238 m asl. The top of the hill was cut by human works and its perimeter was protected by basalt counterforts. From this position, a 360° view is possible, in order to control all the island and its landing sites. The importance of this settlement is testified by lithic findings in the style of Capo Graziano (Eolie islands), and by the presence of a necropolis with "grotticelle" tombs in which ceramic findings from the same age were recovered.

The most populated settlement of the prehistory of Ustica was built during the Middle Bronze Age, the Faraglioni Village, that is located on the edge of a 20 m-high cliff overlooking the northern coast of the island, in the Tramontana sector. This sector of coast, formed by the columnar lavas of the Gorgo Salato and Tramontana, was affected by repeated collapses. The site was choosen because it is well-protected by the sea cliff. Maybe also its sudden abandonment, just two or three centuries after its foundation, is related to the topographical and geomorphological setting.

#### HUSH (Hiking in Urban Scientific Heritage): Augmented Reality as a tool to explore the geological and naturalistic richness of urban areas. An example from Perugia

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Keywords: Geotourism, Augmented Reality, Urban areas.

In the past two decades, geotourism has increasingly become an important channel for promoting geological knowledge and diversifying the tourism industry, also in urban contexts (Del Monte at al., 2013). The recent advancements in Augmented Reality technologies create the basis for the development of immersive geotouristic experiences. Urban geotourisim and Augmented Reality are the key elements of the HUSH project. Its first focus is the identification of the geological (mainly lithological and geomorphological) and naturalistic (faunistic and vegetational) components in a given urban area, through literature surveys and scientific research. The choice of taking into account both the biotic and abiotic aspects is based on the increasing scientific awareness of the interplay between Biosystems and Geosystems (Musila et al., 2005). These components come to be Points of Interest (PoI) along touristic paths, where they are connected to the historical and artistic components of the area. Augmented Reality is the mechanism by which the user can access these contents, by means of a mobile application. In the geodatabase, each PoI is defined by a target image. This allows the user to access the augmented content by framing the target element for the component with their mobile device. The contents are delivered as videos, text, images, or interactive 3D models. Additional functionalities are embedded in the front-end mobile application in order to accomplish several tasks: (i) The access to the PoI can be performed in different ways. With the goal of personalizing the experience, the user has the possibility to choose between predefined paths, paths suggested according to a keyword-based search, and "intelligent paths" based on a Deep Neural Network (DNN), which is able to perform an automated association between user profile and PoI characteristics embedded into specific metadata. (ii) The information flow is not unidirectional, the user can act as a scientific reporter sending their feedback or submitting new contents for examination by the research group. This allows increasing the detail level of each PoI, and the network of information to grow over time based on the user experience fulfilling the "citizen science" paradigm. (iii) In order to sustain local economy and bring the tourist closer to local realities, information about commercial activities, associations and events based on user location is available.

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## Geological risk evaluation and anthropogenic deposits in Rome (Italy): potentialities from an interdisciplinary approach

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Keywords: anthropogenic deposits, geological risk, Rome (Italy).

In historical urban centers, risk evaluation requires a deep knowledge of the subsoil. Because of the high value of the cultural heritage that might be damaged, and the high vulnerability of the aged constructions, the risk may be high even in case of low geological hazards. To assess geological hazards, a geological modeling is mandatory, and studies need to be suitable to this aim. For urban planning purpose, new investigations are expected to be cost and time dependent, and their execution is prevented by logistical and legal factors. Conversely, the examination of results from previous geological studies and investigations might provide sufficient knowledge.

Anthropogenic deposits are one of the key factors to be investigated. Especially in historical centers, they are spread in frequently thick layers, whose sedimentological, hydrogeological and geomechanical characteristics vary, even in the same site, as in no other geological unit. Generally, such deposits are geotechnically weak and may amplify seismic ground response. For these reasons, their site characterization requires specific investigation, whereas for planners a trustworthy model of just their spatial distribution might be satisfactory. However, the available borehole logs, which represent the main source of such information, are generally insufficient for an adequate modeling because of their low spatial density and bad distribution. For historical urban sectors, an opportunity to collect more information regarding topographic modification related to human activities, and to estimate thicknesses of anthropogenic deposits is given by interdisciplinary approaches. Being the archeological investigation mainly performed within those deposits, the examination of such reports may provide information useful for anthropogenic units. Morever, the GIS-supported multitemporal analysis of historical maps is essential for the comprehension of more recent landscape modifications.

Sometimes even at the project level, such interdisciplinary data and further information might be sufficient for the implementation of a preliminary design of the project, and to address choices regarding the location and type of investigations that are required for subsequent design stages. We present results from the application of such a methodology in a geologically-, archeologically- and historically-key urban sector of Rome. In addition to the above mentioned interdisciplinary analyses, many historical, geological and archeological academic papers were re-examined, together with historical cadastral notes from the central archive of the municipality. Moreover, the survey in historical buildings of structural damage cracks, whose geometry can be tentatively related to differential settlements of foundation soil, was performed. The integrated examination of the collected data let us confirm the cogency of the preliminary geological model, so evidencing the potentiality of such a methodological approach.

#### Landscape: a neglected ace in the hole

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Keywords: Landscape, Geoheritage, communication.

We are Living in the Anthropocene, an Era characterized by technology and virtual reality, where all is superficial and fragmented as a broken mirror surface: new and unconventional strategies in communicating sciences, are now essential. An important objective, referring to Geoheritage and its social aspects, is represented by the promotion of concrete actions to restore, protect and sustainably exploit those areas characterized by geo/environmental settings worthy of special protection. Landscape is the key to start a social involvement in a balanced territorial management, aimed at enhancing resources, as well as at preventing risks. Being an object of human perceptions, Landscape becomes a "medium" to communicate Earth Sciences to the whole society. Each individual landscape, studied at different scales, shows distinctive elements: structural, functional, dynamic (Amadio, 2003): in such terms, each landscape can be analyzed in different ways. Modern cartography and GIS are the best tools to represent and communicate the complexity of the territory. These initiatives, aimed at sharing geological knowledge, are successfully started thanks to a synergy between the Camerino University and the Geological Survey of Italy-ISPRA. Landscape is here used to transmit scientific information to a mass audience, inserting the themes of Geoheritage and sustainable development, as the challenge for a shared wellbeing.(Farabollini et al., 2014) - The geological characterization of the Landscape in movies and fictions, is an experience based on the use of the filmic communication, aiming at making the territory comprehensible to the whole society. In the episodes of the famous TV series "Il Commissario Montalbano" filmed in Sicily, the natural and cultural landscapes, giving a fascinating scenery to the films, represent a meaning in the representation of history (Lugeri et al., 2015). - The "GeoloGiro" is a project for the popularization of scientific knowledge explaining the geological setting of the landscapes crossed by the cycling race "Giro d'Italia". The morphology of the territory becomes a key component in the race context; explained by the geologist, it offers to the public a new and interesting point of view of the landscapes, linking scientific information to the agonistic value of the stage. (Lugeri et al., 2018) -The GiROSAuro is a cartoon created for the youngest audience, dedicated to the largest public. A dinosaur, cycling and pink like the jersey of the "Giro d' Italia" winner, explains the secrets of geology, telling us how everything is always changing. The "LandscApp" is a smartphone App realized by ISPRA in an experimental way, a social tool useful to make the users understand the main geomorphological characteristics of an area, particularly referring to the touristic ones (Lugeri et al., 2017).

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#### The "Perugia Upside Down": an exhibition to promote the Urban Landscape

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Keywords: Urban Geology, Exhibition, Education.

In the Umbria region (central Italy) despite a great geodiversity that characterizes the region the most important towns in terms of historical, cultural and artistic reasons have a common geological setting. They are all placed on the top of the hills bordering the rare flat areas of the region. Pliocene-Pleistocene fluvial and lacustrine sediments, displaced by the Quaternary extensional tectonic phases, form the hills. The lowlands are intermontane basins related to late Quaternary river valleys calibrations. Perugia is one of these towns and, being the capital city of the Umbria region, is an ideal example for testing new ideas to promote the Urban Geology.

Perugia is located on the top of a triangular shaped hill (maximum altitude value 493 m, minimum value 171 m a.s.l. and areal extent about 27 km2), along the western boundary and in the middle portion of the Tiberino Basin, the widest intermountain basin of Umbria. In the sedimentary sequence of the hill conglomerates, sands and clays are placed in lens with frequent heteropic contacts and it is the result of the complex interaction between the basement initial topographic arrangement, the recent tectonic evolution and the depositional/ erosional phases common to the entire Tiberino Basin. The shape of the hill is summarized as "ridges and empty spaces" pointing to two fundamental morphological elements of the relief: ridges and streams. Moreover even if Perugia is located on fluvial deposits it is surrounded by rocky reliefs; over the centuries these rocks have provided construction stones for the most important civil and religious monuments: travertine for the etruscan age, the pink and white calcareous stones together with the sandstones in the Medieval Age. After the Unity of Italy, the use of terracotta in Perugia was very common for building decoration. Some chimneys in various districts of the city recall the activity associated with the manufacture of clays outcropping on the hill.

Due to the great cultural heritage related to the geological component an exhibition named "Perugia Upside Down" was done (started on 10 November 2017 and ended 10 June 2018) in the POST Museum (Perugia Officina della Scienza e della Tecnologia). In the exhibition 5 sections were present: the first was dedicated to the Geology, the second to the Geomorphology, the third to the link between the human settlement and the landscape, the fourth to the stones used for the most important historical buildings and the last to the paleontological heritage discovered in Perugia at the beginning of the twentieth century. Panels and exhibits were showed.

The exhibition recorded an extraordinary turnout of the public and was a unique opportunity for the dissemination of the geological heritage of Perugia.

### Following Carlo Levi: a geological itinerary within the "Matera-Basilicata 2019, European Capital of Culture" Events

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Keywords: Carlo Levi, Geotourism, European Capital of Culture 2019.

On 17th October, 2014, Matera, a mesmerizing small town in southern Italy, was designated as European Capital of Culture 2019 This prestigious designation may offer the perfect opportunity to divulge the culture of geology, especially to non-expert audiences. In fact, Matera, a UNESCO World Heritage Site since 1993, devoted to cultural tourism, could be a driving force for the less known internal areas of the Basilicata Region within which Matera is administratively located. On this regard, the local institutions could organise touristic field trips containing thematic tours (historical, literary, archaeological...) coupled with geological information.

Here is proposed a sample itinerary which touches upon three towns, all situated within the province of Matera, and connected to one another not only because they are the setting of Carlo Levi's political exile in the 1930s, but also because each town lies within one of the three important orogenic elements characterising the geology of southern Italy: the Apulia Foreland, the Bradanic Trough, and the southern Apennines Chain. The proposed itinerary sets off from the town of Matera, located within the Apulia Foreland, continues through the small town of Grassano, located within the Bradanic Trough, and ends in the small town of Aliano, located within the southern Apennines Chain. Matera has already achieved international notoriety, also due to its geological features, and in particular for the the *Sassi*, a prehistoric troglodyte settlement consisting of peculiar *cave houses* dug into calcarenites. Rocky walls of *Cinti* at Grassano could be considered both for promoting the study of an ancient settlement of the Knights of Malta, as well as understanding the geological evolution of the Bradanic Trough. Indeed, tourists can admire the long cellars dug out of sandy-conglomeratic deposits, crossing a *gallery exhibition* of an ancient deltaic system. Ultimately, the more sensitive tourist can experience the melancholic charm emanated by the badlands which lead along the Agri River towards the cliffs at Aliano.

During his exile, Carlo Levi narrated and described these three places through his paintings and renown book *Christ Stopped at Eboli*. In his works, Levi captured both the human aspects, as well as the historical and geological ones. A selection of Levi's artworks can be utilized to guide tourists along the journey, illustrating the geology of the area through the eyes (i.e. the paintings), and, above all, the words (i.e. the book) of Carlo Levi. Therefore, the Literary Park constituited in the area and dedicated to the writer/artist could be enriched by geological keys of landascape reading.

## Peri-urban areas, morphological evolution and hazards: The case of Rio city, Northern Peloponnese, Greece

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Keywords: Peri-urban areas, Rio, Peloponnese, hazards, morphology, evolution

Morphological evolution and its relationship with peri-urbanization is becoming an increasingly interesting and significant topic, due to the high impact that it has on highly sensitive areas.

Our study area is the city of Rio in northern Peloponnese, located approximately 7 km from the city of Patras. With a population of around 15.000 people, is considered to be a highly sensitive area, because of numerous and important infrastructure, such as the University of Patras, the local University hospital, two sports halls and the Ottoman era fortress located at the coast.

The geology is characterized by the formation of Olonos – Pindos zone, including Pliocene and Pleistocene sediments, covered by quaternary and alluvial deposits (Tsiambaos, Sabatakakis & Koukis,1997; Rozos, Koukis & Sabatakakis, 2006) and faults of NE-SW and NW-SE direction.

Geochronological and sedimentological studies of dated raised terraces (Doutsos et al., 1988; Stamatopoulos et al., 2004; Frydas et al. 1995) found an average uplift rate of 0.4 to 6 mm/yr (Stamatopoulos et al., 2004) while the dating results indicate pre-Tyrrhenian to Tyrrhenian interglacial ages.

Hydrologically, the area is characterized by ephemerous streams and rivers such as Charadros, Selemnos and Volinaios, flowing into both the Gulf of Patras and Gulf of Corinth. The area combines sectors of mixed use. Green parts are also present in a currently developing area.

During the years, the area has undergone a series of changes that can be developed into potential hazards. The construction of Patras University in the 1960's and the University hospital in the late 1980's led to the infilling of one branch of Selemnos river, increasing the risk of flooding of the remaining river branch.

The coastal area suffers from erosion introducing risks to the port and coastal infrastructure. Some minor remediation works were unsuccessful. Combined with the high seismicity of the area, the extensive human intervention, high seismicity and the local tectonics, introduce risks that have to be researched, studied and controlled.

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### Morphological evolution of the urban landscape of the city of Patras and possible natural hazards

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Keywords: Urban development, city of Patras, Peloponnese.

The man-land relationship is complex problem. Geomorphological changes, stimulated by allogenic inputs have to be studied in order to explain how the environment we live in was created and the systems that reacted with each other to give todays physical surroundings.

This work explores the interconnection between geomorphology, human intervention and urbanization. We attempt to explain and analyze the behavior and combined interaction of the already existent landform. Consequently, we try to quantify the possible geomorphological risks that the urbanization of the study area poses in combination with the city of Patras growth.

Patras, the regional capital of Western Greece, is Greece's third largest city with a population of around 270.000, located in Northern Peloponnese. It is built at the foothills of Panachaiko mountain, characterized by Mediterranean climate. The study area has a size of c. 12 km<sup>2</sup> The history of the city spans over 4.000 years, with the first indications of inhabitants coming from the prehistoric age, while it was founded in the 11<sup>th</sup> century BC.

The geological basement of the surrounding area is of the Olonou - Pindou geotectonic zone. Pliocene/ Pleistocene sediments are present, and most of them covered by quaternary and alluvial deposits (Tsiambaos, Sabatakakis & Koukis,1997; Rozos, Koukis & Sabatakakis, 2006).

Tectonically, the area is characterized by two groups of normal faults, of NE-SW and NW-SE direction and is also characterized by high seismicity (Tsiambaos, Sabatakakis & Koukis, 1997).

One of the most important features of the city of Patras is its' port which has rich history and has been

heavily modified during the years. It's a part of Patras Gulf which is a microtidal sea dominated by locally generated waves (Piper et al., 1982; Alevizos & Stamatopoulos, 2016). The first indications of maritime and coastal activities during the prehistoric ages have been located in the area of Agia in the NE of the city.

Finally, the drainage network of the study area mainly consists of three rivers, all flowing in the Gulf of Patras, Diakoniaris, Glafkos and Milichos which have created problems in the past with catastrophic floods. Especially the stream of Diakoniaris is one of the most catastrophic overflowing rivers in Greece (Despiniadou & Athanasopoulou, 2006). Land use and the development of the city of Patras, especially in the mid 1800's and even greater in the 1950's have led to the encasement of both Glafkos river in the 70's and Diakoniaris in 2000's.

In all mentioned cases, this urbanization of Patras, the local geology and tectonics, the landforms and local geomorphology and the correlation of these factors, formed the city but also introduced risks that have to be studied. Human intervention and man-made landforms were located along with morphological changes. These changes combined with the hydrological ones and also climate change, increased the risk in the city of Patras in terms of hydrology and geology.

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### Anthropogenic tuff cavites in the southern metropolitan area of Caserta (southern Italy): hazard evaluation vs. Enhancement of the territory

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Keywords: artificial cavities, geology, hazard.

The Late Quaternary geological evolution of the northern Campania Plain (southern Italy) was affected by the volcanic activity of the Phlegrean Field. Among the volcanic events that have characterized this area, the ones that emplaced the Neapolitan Yellow Tuff (NYT) and the Campanian Grey Tuff (CGT) were the most important. Since the tuff has good mechanical properties, it was involved since historical times in an extensive mining activity, from which a very dense network of underground cavities was inherited, strongly related to the lithofacies distribution.

The habit of man to excavate artificial cavities in the above area began long time ago and it is well known in Naples. In many urban centers north of Naples cavities have been reported as well in specific geological investigations, although their real extent is almost unknown. In these towns the underground mining activities were performed to extract tuffs for buildings. The urban development have sealed every signal of the presence of cavities, which thus represent a geological hazard and contribute to subsoil instability of many places.

The present study is a first attempt in providing a geological underground database and a preliminary analysis of the hazard aspects related to the mining activities recognized in the metropolitan area of Caserta, north of Naples.

First step of the investigation was the reconstruction of the main geologic features of the study area based upon lithostratigraphic logs from boreholes, available from different sources. The marker key to correlate the different units was represented by the CGT deposits.

A GIS project was then designed to manage a georeferenced cavity database and plot the cavity distribution on the numerical cartography. Where available, cavity plan views were collected and managed in GIS environment to outline the extent of hypogean distribution. The knowledge of such an hypogean system could be a useful contribution to the hazard evaluation in the considered densely urbanized area and will provide the local governments information for the civil protection and urban planning activities.

All of these underground structures have the potential to be used in a manner that will contribute much more to the current culture of the towns (i.e. they could be used as concert halls, museums, galleries, exhibition areas, restaurants and touristic facilities). A further investigation concerning the physical status of the cavities is thus desirable in order to carry out monitoring on their conditions of stability and the state of deterioration, with the aim to combine and integrate preservation, management and protection of the underground cultural heritage.

## Session S37 Geoparks and geosites: tools for knowledge and protection of geological heritage

Conveners AND CHAIRPERSONS Pietro Marescotti (Università di Genova) Rosolino Cirrincione (Università di Catania)

## The relationships between Geosites and nature reserves: The case history of the Karsts systems managed by Cutgana (University of Catania)

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Keywords: Hyblean Foreland, Geosites, Karstic systems.

Seventy-six new geosites have been established inside some sicilian nature reserves on recent times (D.A. n. 283/2017, published on 29 august 2017, G.U.R.S.). Three of them are located inside the Syracuse administrative territory and are managed by Cutgana (University Centre for the Protection and Management of Natural Environments and Agrosystems) belonging to the University of Catania.

These geosites are rappresented by the "Complesso speleologico Villasmundo - S. Alfio", the "Grotta Palombara" and the "Grotta Monello", the same denomination of the nature reserves in which they are. The reserves represent epikarstic systems with interconnected karstic conduits and galleries within the Mt. Climiti Formation (Lower - Middle Miocene).

The "Grotta Monello" geosite is located inside the SIC ITA090011. It is a system of chambers and galleries about 540 metres in lengths. The pecularities of the karst system is the massive occurrence of stalactites and stalagmites often forming columns having at places decametric dimensions.

The "Grotta Palombara" geosite is located in the territory of Melilli (SR) inside the SIC ITA090012. It is composed by a system of galleries and conduits 800 metres in length connected with the ground surface through a 12 metres deep pit hole measuring 15 metres in the maximum dimension. The epikarstic morphologies are here good developed with the occurrences of sinkholes showing a decametre scale diameters.

The "Complesso Speleologico Villasmundo - S. Alfio" geosite is located close to Melilli (SR), inside the SIC (ITA090024) of the Nature 2000 Network. The karstic system is mainly represented by two galleries, the Villasmundo and Alfio caves, partially filled by underground water, and developed 2.5 kilometres and 400 metres in lengths, respectively. The Villasmundo Cave is a succession of tunnels, sinkholes and pits until the spectacular "Terminal Lake".

### Majella National Park international geosites: identification, list and challenges for conservation

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Keywords: Majella, Geopark, Central Apennines.

Majella National Park (MNP), aspiring UNESCO Geopark, is located in the Central Apennines (Italy). Its territory covers a mountainous area of about 740 km<sup>2</sup>. The main relief of the Park is the Maiella Massif, an arc-shaped asymmetrical anticline gently plunging towards NW and SSW. In correspondence of the fold axis culmination an alignment of carbonate peaks exceeding 2,500 metres in elevation is spectacularly exposed.

From a geological point of view the territory of the MNP is one of the most interesting regions of the Central Apennines. The complex geological history of the Maiella Massif and surrounding areas closely matches the unusual geomorphological heterogeneity of the territory. In fact, a variety of different landforms, resulting from a combination of karst, glacial and fluvial processes, characterizes the territory. Bare pitted highlands shaped by flowing ice that long ago covered the higher parts of the massif, similar to lunar landforms, characterize the top of the Maiella (es. Vallone di Femmina Morta). Impressive narrow canyons (es. Vallone dell'Inferno) sided by vertical cliffs cut across the Maiella exposing thick sequences of basinal and platform-derived carbonates. Wide sunny karstic plateaux covered by Olocene lacustrine deposits (es. Quarto di Santa Chiara at 1,250 m a.s.l.) are interposed between the NW-SE elongate reliefs of Rotella, Pizzalto and Porrara. Finally, a wide tectonic depression like the Caramanico Valley (carved by Orta River) separate the rounded gentle profile of the Maiella Massif from the impervious steep slope of the Morrone.

The Park also preserves evidence of how much the geological features can be deeply fused with cultural inheritance. The first human presence date back to the Early Paleolithic (600.000 years ago) as testified by the stone tools recovered in lacustrine deposits at Valle Giumentina. Since the Medieval period and until the last century many human activities, like eremitisms, agro-pastoral practices and mining, left evident signs on the landscape.

In this framework, 95 are the geosites that have been currently identified and some of these (21) are wellknown to the international scientific community. Every year several Italian and foreign researchers visit Maiella for their scientific programs and educational field trips. Owing to the well-preserved Platform-to-Basin Carbonate System, the Maiella Massif acts in fact as a model for the hydrocarbon genesis and oil migration.

Among the aims of the MNP is to catalogue and include all the data concerning its sites in the ISPRA Geosite Database. The main goal, however, is to make these geosites known to the public, including local administrators, operators, guards, inhabitants and geotourists. In fact, many are the natural and the anthropic threats that can compromise the integrity of a geosite. The mere knowledge of their existence and importance is the first step for removing any risk of losing the site forever or of compromising its fruition.

## The world geosites of Sicily: the state of art

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Keywords: Geological Heritage, World Geosite, Sicily.

The term geosite refers to the geological, geomorphological, palaeontological, mineralogical and other interests in a territory with scientific and environmental values of the landscape heritage (Wimbledon et al., 1996). Generally, geosites are natural architectures, or singularities of the landscape, which testify to geological processes that shaped our planet, and represent cultural and recreational attractions.

With the regional law 11 April 2012 No. 25 and the subsequent decree of the Department of Territory and Environment (D.A. n. 87 of 11/06/2012), Sicily adopted a specific regulation for the establishment of the "Regional Catalog of Geosites".

Six years after the promulgation of the regional law, the Sicily Geosite Catalog includes:

- 93 "Geosites" created in Natural Reserves of geological interest (D.A. 283/2017),
- 15 "Geosites" set up with the aforementioned decree,
- 6 "Geosites" instituted;
- 350 "Sites of geological interest" (which will be progressively established),
- About 2000 "Warning Sites" (sites whose rarity and representativeness requirements have to be confirmed by multidisciplinary studies to be subsequently included in the "Sites of geological interest").
   Among the decreed Geosites, twelve are of world importance:
- GSSP del Piacenziano Punta Piccola, Porto Empedocle (Agrigento) (D.A. 103/2015);
- Grotta Rumena 1 Custonaci (Trapani) (D.A. 104/2015);
- Lave brecciate a fluoro-edenite e fluoroflogopite di Monte Calvario Biancavilla (Catania) (D.A. 105/2015);
- Salinelle System of Mt Etna:
  - Area 1. Salinelle dei Cappuccini Paternò (Catania), (D.A. 581/2015),
  - Area 2. Salinelle del Fiume Paternò (Catania), (D.A. 584/2015),

Area 3. Salinelle di San Biagio - Belpasso (Catania) (D.A. 96/2016),

- Travertino della Cava Cappuccini Alcamo (Trapani) (D.A. 586/2015),
- Duomo endogeno riolitico di Basiluzzo Isola di Basiluzzo, Panarea (Messina), (it falls in the Panarea Island Nature Reserve and nearer rocks),
- Terreni del Permiano-Trias della Valle del Sosio Palazzo Adriano (Palermo) (D.A. 86/2017),
- Sistema dei Diatremi degli Iblei settentrionali (Sicilia sud-orientale): Diatrema di Valle Guffari - Buscemi (Siracusa), (D.A. 436/2017), Diatrema di Costa Giardini - Sortino (Siracusa), (D.A. 80/2018),
- Il sill basaltico triassico di Contrada Vignale Leonforte (Enna).
- Wimbledon, W.A.P., Andersen, S., Cleal, C.J., Clowie, J.W., Erikstad, L., Gonggrijp, G.P., Johansson, C.E., Karis, L.O., Suominen, V. (1996): Geological World Heritage: GEOSITES - a global site inventory to enable prioritisation for conservation. Mem. Descr. Carta Geol. d'It., 54(1999), 45-60.

# The Aspromonte GeoPark (Calabria, Southern Italy). Enhancement and popularization of geosites by means of new digital technologies

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Keywords: Aspromonte GeoPark, new technologies, geosites popularization.

In the Aspromonte National Park many geosite are been recently proposed and classified.

Many of them have an international interest and are listed in the world geological heritage.

The Department of Biology, Ecology and Earth Sciences (DiBEST) of the Calabria University has recently contributed to the proposal of new geosites present in the Aspromonte National Park.

In the last year, many conferences, field trips and lessons were organized by the DiBEST, by the Aspromonte GeoPark Office and other Institutions in order to promote these abovementioned geosites and the candidacy of the Aspromonte Park to the UNESCO Global GeoParks.

For the next future, a lot of new technological tools for the touristic attraction could be planned and are here proposed:

- "TGeosites". It consists of a series of geological video for television or web (like a scientific TG) which could explain each classified geosite in a easy way; that is, the video-commented Geosites Inventory Cards.
- "AspromonteGeoDocuApp". It consists of an Android/Ios application available for smartphones and tablets, that provide an innovative online database on the geological-stratigraphic-geomorphologicalpaleontological-ichnological aspects of the Aspromonte mountain. This particular App will be accompanied by textual information, photographs, geological audiovisual documentaries addressed to visitors, tourists, trekkers, researchers, students and local people.
- "WalkieParkTalkie". A park of walkie-talkie available for tourist and trekkers for the maintenance of safe communication in some area of the Aspromonte Park not reached by the cell towers.
- "GeoArchaeoNavigator" connected to the classical TomTom/Garmin/GoogleMaps/etc., able to inform tourists in real time about the presence along the way of particular geological or archaeological attractions in the Aspromonte National Park.
- "AsproComics". That is, original comic books to expose and popularize the local geology and paleontology to children. For example, the geosite Pietra Cappa could became the Talking Rock (animated protagonist) that tell his long geological history! Furthermore, geological cartoons and videogames could help the popularization of the Aspromonte GeoPark among the young people.
- At the same time, a good way to promote the Aspromonte Unesco Global GeoPark is the organization of:
- periodical field trips (not only for Researchers and trekkers but also for school students of all levels);
- geo-marathons (like triathlon routes along the geosites);
- legal and safe bungee-jumping from mountains edge;
- ludic-scientific days (a series of "Eat-Drink-Learn" GeoConferences, taking place maybe in winebars or in pizzeria- restaurants) addressed to the general public.

### The Triassic sill of "Contrada Vignale" (Rocca di Cerere Geopark, Enna, southern Italy)

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Keywords: Geosite central Sicily, Triassic sill, Pangea breakup.

In Central Sicily, inside the Geopark "Rocca di Cerere" of the European Geoparks Network and the natural reserve of M.te Altesina, a sub-volcanic basaltic body crops in locality "Vignale" of Leonforte Village (N 37°38'25" E14°19'40").

The sill was emplaced in the middle-late Triassic and it is a unique and significant geosite since it represents the only known evidence of a segment of the Triassic rift system associated with early stages of continental rifting processes in Central Sicily.

The break-up of the supercontinent Pangea is the global geologic event in Mesozoic times. In response to lithospheric extension, magmatic activity related to partial melting of upper mantle took place, initially producing alkaline magmas.

The sub-volcanic body consists of a sill of a thickness up to 25 m; the color is gray and the microstructure holocrystalline, with fine- to medium-grained portions moving toward the inner parts of the body.

A late Ladinian-early Carnian age (~ 240-230 Ma) has been assigned to this intrusion. These rocks have an alkali basaltic composition and show OIB-like incompatible element patterns in primitive mantle-normalized diagrams (Kawabata et al. 2011) (e.g., enrichnments in HFSE and LREE coupled with high HFSE/LILE ratios), as well as slightly positive eNd values. Geochemical features clearly suggest a within-plate, anorogenic, tectonic setting..

Their characteristics are very different compared with the Permian calcalkaline magmas from elsewhere in SW Europe still carrying the geochemical signature of modifications related to the Variscan Orogeny. Furthermore the mineralogical, geochemical and isotopic composition of these products are different from the coeval volcano-plutonic formations of Southern Alps.

The sub-volcanic body, if compared with the anorogenic rocks of similar composition, emplaced in the same geodynamic context in other sectors of the SW Variscan European chain (Orejana et al. 2008), suggests a common origin related, at least in part, to the tectonic collapse of the Variscan Orogen. The magmatic rocks of Central Sicily provide evidence of the sodic alkaline magmatism associated with the intra-continental extensional processes and crustal thinning that, following the collapse of the Variscan Orogen, characterized the earliest stages of the break-up of Pangea.

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#### First results from Evaluation of the Carrying Capacity of the Monello cave

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Keywords: geosite, cave, karst.

The scientific research "*Evaluation of the Carrying Capacity of the Monello Cave*" is aimed at evaluating the carrying capacity in the hypogeous part of the "Grotta Monello" Natural Reserve. The carrying capacity indicates the maximum number of visitors (sustainable tourist flow) that a natural system can accommodate without significantly altering the environmental parameters. To quantify the carrying capacity of a karst cavity, the energy level of the cave system must be considered in general, with a particular focus on the relationships between the energy level of the cavity and the energy flow introduced by visitors inside the cave.

The Monello Cave, which has a total development of 540 m of which 160 m easily visitable

and 380 m explored, is a karstic hypogeum, rich of stalactites and stalagmites and concretions of different sizes having a moderate flow of energy.

In the first phase an environmental monitoring plan is being carried out in two different detection stations, with a duration of three years. Measurements of  $CO_2$  content, temperature, humidity and air currents in relation to a variable number of visitors are already in progress. Measurements of environmental parameters are carried out in the absence and in the presence of visitors, with measurement cycles lasting a few hours.

The data collected until now reveal interesting information regarding the extremely variable  $CO_2$  values and the particularly stable values of the temperature inside the cave.

In the second phase it is planned to use tools for long-term measurements in order to evaluate the possible incremental increase of the effects of the load inside the cave, which is not detectable in the individual measurements.

At the same time, the artropodofauna living in the Monello Cave will be monitored. A qualitative and quantitative survey will investigate the populations of the troglobial species *Armadillidium lagrecai*, *Glomeris dionysii*, *Chthonius multidentatus* and *Roncus siculus*.

### The peculiar features of the "System of the Salinelle of Mt. Etna" Geosite (East Sicily, Italy)

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#### Keywords: Mud volcanoes, Mt. Etna, Thermal waters.

The so-called "Salinelle of Mt. Etna" are natural manifestations with emission of fluids and also formation of mud volcanoes, which occur near the town of Paternò. They occur in three sites: the Salinelle of Capuchins or of the Stadium (Paternò), the Salinelle of the River (Paternò) and Salinelle of Vallone Salato or of San Biagio (Belpasso). These sites are characterized by the emission of highly saline water, generally at ambient temperature, accompanied by emission of mud, gas and liquid hydrocarbons. The peculiarity of these sites lies in the fact that the emitted fluids, unlike other similar sites around the world, formed from the admixture of magmatic/hydrothermal gas, which makes up the bulk of the gas phase emitted, with sedimentary and crustal gas. This produces unique landforms, with bland relief, caused by the emission of an abundant liquid component without the clay fraction (other mud volcanoes in Italy and around the world typically have emissions with prevailing mud or muddy water), also due to the condensation of high-enthalpy fluids of deep magmatic origin. For these reasons, the output of fluids at the Salinelle is strongly bound up with the changes in the deep volcanic activity of Mt. Etna, leading to production of paroxysmal eruptions, often spectacular, normally accompanied by emission of thermalized waters. This makes the Salinelle interesting also for volcanological and geothermal studies. In addition, the emission of fluids is continuous, in contrast to what happens at other similar sites. Finally, the rarity of geological phenomenon and its extension, as well as its geomorphological interest, is coupled with the fact that the site is an excellent example of pseudo-volcanic phenomena and produces very different and peculiar morphologies. These features make the Salinelle of Mt. Etna almost unique in the worldwide panorama of mud volcanoes, because normally the gas that guides the ascent of mud and water in this type of natural events is composed almost entirely of methane and other hydrocarbons. This was the main reason that led to the recognition of the Salinelle of Mt. Etna among the Geosites of world interest, to be protected and studied in detail.

#### The Cortabbio-Primaluna barite mine (Valsassina, Lc): emotion, experience and disability

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Keywords: barite, underground mine, geotourism.

The Alps have long been a major mining area, with a large diversity of ore deposits and mining activities, related to the complex geologic history of these mountains. The increasing interest for the preservation and divulgation of the mine geoheritage of this area has led in the last decades to rehabilitation and re-opening, as geotouristic sites, of several old mines. The Cortabbio-Primaluna mine, on the eastern slope of Mount Grigna, in the Southalpine tectonic domain, has just been added to this diversified offer as a unique geoheritage site, both for its geologic and mining peculiarities and the novelty of geotouristic approach developed.

The main barite body is related to a system of hydrothermal veins extending for 1200 m in length and up to 200 m in width, with a maximus thickness of 8 m. They cut the paragneiss and micaschists of the Southalpine Paleozoic basement, very close to its contact with Permian porphyries.

At Cortabbio-Primaluna, a small outcrop of barite was discovered in 1860. Open stope underground exploitation of the barite ore, that started soon after, lasted till June 2012. The surviving of the mining activity till very recent, a very rare occurrence in the Alps, allowed to very efficiently set up a plan for re-opening as a geotouristic site of a mine that did not undergo the degradation typical of long time abandoned sites

The location within the Northern Grigna Natural Park and the collaboration with several more public Authorities, among which the Primaluna Municipality and the Lombardy Region, together with the geotouristic private enterprise "Miniere Turistiche del Lago di Como", favoured the works for securing and opening to the public. Since its opening, in August 2015, the mine has seen an increasing number of visitors and, as far, is the only geotouristic barite mine in Italy.

The presence of a never abandoned, perfectly preserved mine offers visitors the unique possibility to observe a state of the art mining site where mining operations stopped just few years ago. Recently Miniere Turistiche del Lago di Como, in collaboration with Primaluna Municipality and Legambiente, has started a pilot project for the preparation of routes especially designed for people with motion and visual disabilities. The routes, expanding both inside and outside the tunnels, are developed as sensorial and emotional experiences, that, involving different senses, enrich the visitor with a deeper insight into geoheritage. They are also supported by virtual reality routes that cover the portions of the mine not accessible to motion disabled visitors, while visual disabled visitors tour is integrated by specially designed sensorial experiences.

The opening to the public of the Cortabbio-Primaluna mine makes the Valsassina mining district, comprising also the geotouristic lead and zinc mines at Pian dei Resinelli, a valid candidate either for a UNESCO Geopark or a Mining Park application.

# The contribution of the "Environmental Interpretation" to the communication and scientific divulgation of the Geological Heritage: the case of the Aspromonte Geopark Project

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Keywords: Geological History, Earth Science divulgation, Memory of the Earth.

The Geological Heritage concept was expressed for the first time during the International Declaration of the Rights of the Memory of the Earth in 1991 at Digne des Bains: "The difficult story in the history of the Earth lies in the rocks and the landscape recognizable at its surface; these represent the *Memory of the Earth*. Only in these sites, and only there, it is possible to trace the processes that have occurred in thousands of millions of years and which have created the current aspect of our planet, including the evolution of life in which man is inserted".

What is preserved in the rocky outcrops and in the landscape is then to be considered unique and, at times, very fragile.

For this reason, it is necessary to reflect on the fact that what is lost in this heritage can be never restored or rebuilt, and it is therefore necessary to understand and proceed with its protection.

The main aim of the Declaration is therefore the conservation of the Memory of the Earth kept in the *Geological Heritage*. Thinking, however, of being able to safeguard something that is unknown is rather difficult and illusory. The path to be follow, therefore, is that which, from research and scientific knowledge, passes through the *Interpretation* (Tilden F. 1957) and *Translation* of the technical language of the Earth Sciences into messages that can be understood by *non-professionals*, for to favor the dialogue between the scientific community and the common people.

This is even truer the more the *Memory of the Earth* is enclosed in a protected area and/or in a Geopark, in whose concept of management the holistic approach to protection, education and sustainable development is inherent.

In this view, the interpretation of the geological landscape have to be focus its attention not on a single scientific notions, illustrating facts and isolated data, but on themes that meet the curiosity, imagination, interest and liking of those who receive them.

The results are *good experiences* of knowledge of the *book of the earth*, feelings and emotions of amazement and wonder about the birth and evolution of a territory, starting from the geological matrix with the aim to contribute in its conservation and development.

The candidature of the Aspromonte as Unesco Geopark is perfectly in line with the aims mentioned above. Aspromonte is indeed characterized by the presence of rock-types and geological landscapes that tell us an ancient geological history rooted since the Paleozoic with its amazing metamorphic rock outcrops, to arrive up to the recent seismogenic tectonic activity of the Cittanova and Scilla faults, passing through the synorogenic clastic deposition of the Stilo Capo d'Orlando Formation and the evaporitic deposits, which testifies the Messinian salinity crisis.

Tilden, F. (1957): Interpreting our Heritage - Chapel Hill, N.C.S. (USA), U.N.C. Press.

Cirrincione, R., Fazio, E., Fiannacca, P., Ortolano, G., Pezzino, A. & Punturo, R. (2015): Periodico di Mineralogia, 84 (3B).

## The use of aerial and close-range photogrammetry to study dinosaur tracksites both at the meso- and macro-scale: the cases of the Lavini di Marco (Lower Jurassic, Hettangian - Trentino Alto-Adige) and Molfetta (Lower Cretaceous, Aptian-Albian - Apulia) tracksites

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Keywords: ichnology, conservation, sustainable geotourism.

Accurate mapping and 3D models are crucial for studying tracks and tracksites at different scales. The use of small Unmanned Aerial Vehicles (UAVs) for mapping and 3D modelling is becoming increasingly common allowing you to capture reliable and high-resolution images comparable to those obtained by terrestrial laser scanners and manned aerial photogrammetry, but with reduced working costs and rapid execution time.

We used as test areas to evaluate the results of UAV based photogrammetry two well-known Italian dinosaur tracksites: the Lavini di Marco (Lower Jurassic; Hettangian - Trentino-Alto Adige) and the Molfetta (Lower Cretaceous; upper Aptian/lower Albian - Apulia) tracksites. For this purpose, we used different kind of drones with different technical features and parameters and for which we set different flight parameters.

Ground-based photogrammetry on single footprints was also performed, in the light of the recent introduction of high-resolution digital cameras and powerful processing software, with the aim to evaluate its impact on ichnological and ichnotaxonomical and ichnosystematic analyses.

The accuracy of 3D models, DEMs and orthophotos generated by means of UAVs images is extremely high and allows to rapidly map and describe vast and/or hardly accessible tracksites with higher accuracy than that obtained from field data or from digital airphotos

By coupling ground- and aerial-based photogrammetry ichnologists can rapidly obtain consistent and affordable digital models useful to study dinosaur tracksites both at the meso (track) and macro (ichnosite) scale.

The use of this integrated approach can make easier various tasks in ichnological analysis and have direct bearings on ichnological heritage managment: i) large-scale ichnosites description and mapping, ii) field activity planning, iii) in safety investigation of areas with difficult accessibility (i.e., high elevation areas, steep slope); iv) improvement of ichnotaxonomic and ichnosystematic analyses; v) ichnosite conservation and valorisation; vi) development of the prerequisites for sustainable conservation-based geotourism.

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#### Geoscience and education: Proposal of a geo-trail at the Etna Volcano

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Keywords: geo-trail, Earth heritage, Etna.

The present contribution aims to highlight the geological aspects of a path in the southern flank of the Etna volcano. As it is known, Etna is the highest active volcano in Europe and one of the world's most active volcanoes; in 2013 it was added to the UNESCO list, declared as "one of the most documented world records among Volcanoes."

Recently, along the Etnean territory, several trails have been marked by local and national associations; nevertheless, it is worth noting that up to now no signed geological paths have been arranged yet.

The path we propose as a geo-trail is named after the volcanologict C. Gemmellaro and after a large cone (Mt. Grosso), developing for ca. 3 km at an altitude of about 1300 m a.s.l.; here it is possible to admire evidence of various volcanic eruptions that occurred at the second half of the XIX century (1886 and 1892) up to the very recent dating 2001. These eruptions played a fundamental part in shaping the landscape of this sector of the Etna. The trail is peculiar under the geological point of view, since it permits to observe volcanic structures such as hornitos, pyroclastic cones and products, lava flows and channels as well as several types of eruptive rocks exhibiting variations in mineralogical content and magmatic structures related to succeeding eruptions.

Moreover, the XIX century eruptions have been admiringly documented by historians who also reported the close link between natural phenomena and emotional effects on population.

Along the existing path, signposting and way marking are quite rare and in poor stay of repair, despite it is maintained in fairly good conditions.

For this reason, the Piano Nazionale Lauree Scientifiche Geologia project, together with Ente Parco dell'Etna and the University of Catania propose the trail preparation and marking of the meaningful geological sites, volcanic structures and lava flow.

Once complete, the Mt. Grosso-Mt Gemmellaro geo-trail will contribute to promote understanding of the volcanological phenomena that succeed at Mt. Etna as well as to raise Earth heritage awareness in population.

### Geopark in Ferrara: a way to promote geological knowledge

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Keywords: Ferrara geopark, geological exhibition, geological heritage.

Geology is a hands-on, practical subject. Field work is an integral part of geoscience education (Jolley et al., 2018). Van der Hoeven Kraft et al. (2011) defined a component unique to Geosciences, termed "Connections with Earth." In their view, this component plays a role in the motivation for learning Geosciences. It describes the possible ways that people relate to the Earth, including appreciation, wonder, values and aesthetic, it is based upon theoretical and experimental findings and it intersects with peoples' motivation and emotions.

In this spirit, a group of Geology students of University of Ferrara (Italy) conceived the project named "Geologic Park - una scienza da toccare". The fulfilment of this park is economically supported by the "Fondo culturale 2017/2018" of the University of Ferrara and it is already underway.

The role of the park is to introduce visitors to the lithogenetic cycle, in which transformations take place and the rock we can see today takes shape.

The Industrial Design students of the University of Ferrara are currently in charge of designing the park. As the project is a collaboration between Geology and Design students, the processing and the arrangement of the rocks will highlight the potentials of the existing industrial technologies for processing materials and the role that Design plays in the urban furniture.

The project consists of an open-air museum that exhibits a collection of big blocks representing the three general classes of rock: igneous, sedimentary and metamorphic. It will be realized in front of the Physics and Earth Sciences Department, via Saragat 1, Ferrara, in a garden with trees located among some industrial buildings of a former sugar factory, which now are the Technological - Scientific Pole of the University.

The aim is to promote geological knowledge and make the geological heritage known by students and nonspecialist ordinary people. Due to the absence of rocky outcrops in the urban environment of Ferrara, this park represents an important way to make field experience possible.

This permanent exhibition will include labels and panels with geological information about the lithology of each rock sample and barcode tags linking to further explanation. In addition, the park will be furnished with tables and chairs in order to get an outdoor study, reading and meditation space for students and visitors. Moreover, this place will be used for outdoor learning activities such as lectures, seminars, cultural events and so on.

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van der Hoeven Kraft, K.J., Srogi, L., Husman, J., Semken, S. & Fuhrman, M. (2011): Engaging students to learn through the affective domain: A new framework for teaching in the geosciences. Journal of Geoscience Education, 59, 71-84.

## The digital geological map of a treasure chest of geodiversity: the Lavagnina Lakes area (Alessandria, Italy)

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Keywords: QGIS geological mapping, dissemination and outreach, Natural park.

We present the digital geological map of an area located in the Regional Natural Park of "Capanne di Marcarolo" (<u>http://www.areeprotetteappenninopiemontese.it/</u>, Alessandria, Italy), that has a great number of standing features both for its geodiversity and biodiversity. The aim of this work is to illustrate the geodiversity of an area that is not yet a geopark, but that has all the potentiality to become one.

We performed a detailed geological mapping at 1:10000 scale and collected data that have been subsequently integrated into a GIS map as geometries and alphanumeric data. We used Open Source software QuantumGIS, with Qgis2threejs plugin for DEM and 3D model management.

For this work we particularly focused on the Lavagnina Lakes area, that has been studied by several researchers of different branches, focusing on the occurrence of alkaline springs, of floral endemic species and others. This area has driven also the attention of mining companies, because of the gold mineralization and the past gold mining exploitation.

For such reasons this area, beyond the scientific research activity, can also be interesting for geoturism, geoarcheology, outreach for schools, and for gold panning activities.

The gold occurrences were known since the Roman age, and the area was site of mining exploitation with the presence of a metallurgical plant, dedicated to the manufacturing of gold ingots, and a mining village (1589 until the end of 1800). After the depletion of mines, the construction of the two dams, that gave rise to artificial lakes, caused metallurgical plant and the mining village to be submerged.

From the geological point of view, the area is located at the north-eastern boundary of the metaophiolitic Voltri Massif, close to the Sestri-Voltaggio Line, at the contact with the Tertiary Piedmont Basin.

The main remarkable geological features of the area are the occurrence of: i) various lithologies and geologic units derived from different paleogeographic environments: i.e. from the Jurassic oceanic lithosphere, from a continental margin Triassic carbonate platform, and from Eocene-Oligocene sedimentary continental to marine deposits; ii) fossil-bearing rocks; iii) fault systems, characterised by intense and widespread carbonation, that represent the natural analogue of the industrial process of  $CO_2$  storage; iv) gold mineralization; v) serpentinization of ultramafic rocks, important for studing fluid-rock interactions, developed at the ocean floor or in subduction zones; vi) alkaline springs; and vii) geomorphological landscapes.

The databases associated to the map contain all the information that can be interesting from different points of views: i) research (i.e. structures, carbonated fault zone, geomorphology); ii) geoturism (i.e. trail network); and iii) geoarcheology (i.e. mine network).

Our map could be useful both for scientific purposes, and for outreach and dissemination in order to preserve the geo-biological diversity of the area.

## The proposed Geosite "Loddiero Valley" on the Northern sector of the Hyblean Plateau (Scordia, SE Sicily)

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Keywords: Hyblean Foreland, Loddiero Valley, lava delta.

An internationally known, and proposed geosite, is worth to be protected for the enhancement of Sicilian geological heritage. The Loddiero Valley is located in the Hyblean Plateau, which occupies the southeast corner of Sicily and represents the northern flexured edge of the African Plate.

In the area belonging to Scordia village (Catania district), some deeply incised valleys (locally named "cave") cut the stratigraphic succession.

Here, we describe the succession cropping out in the Loddiero valley, which represents the most impressive place to examine the stratigraphic relationships between the Pliocene-Pleistocene tholeiitic and alkalic lavas and shallow water carbonates, and to observe the morphology of an ancient "lava delta". The section is exposed in an abandoned quarry on the left bank of Loddiero Valley, 3 km southwest of the town of Scordia.

The base of the Loddiero section is represented by pillow breccias (pillow fragments in a hyaloclastite matrix) and lesser amounts of closely packed pillow lavas, 7.5 m thick. The pillow lavas dip 25-30° toward the east, and pass upwards to grey, 7 m thick, subaerial lavas, with a fairly horizontal contact. The subaerial lavas comprise pahoehoe flow units, 1 to 2 m thick.

The erosional surface on top of the subaerial lavas is irregular, with up to 0.6 m of relief, and is filled with a basal conglomerate with some pebbles coated with coralline algae. This grades upwards into 3 m of fining-upward succession of bioclastic packstones. The carbonates bear 2 thin dark grey tuff layers. Radiometric dating of the tuff and calcareous plankton biostratigraphy indicate an early Pleistocene age. Overlying columnar jointed dark lava flow, locally with basal pillows intruded into the soft carbonate sediments, close the section at the top.

The succession exposed in the quarry, is an excellent example of the relationships between submarine and subaerial lavas, that suggest the formation of a characteristic "lava delta", with subaerial lava flows entering the sea and building a submarine flow-foot breccia organised in inclined foresets. The contact surface between the submarine flow-foot breccia and the overlying subaerial flows indicates the position of the sea level at the time of volcanic activity. This scenario is identical to the one observed during current eruptions at Hawaii, and reveals the complex interplay of subaerial and submarine volcanism, eustatic sea level changes, and shallow water carbonate sedimentation.

## "Sassi", the old town of Matera in southern Italy: a potential urban geopark in the European Capital of Culture 2019

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Keywords: Sassi di Matera, Rupestrian Town, Urban Geopark.

Recently Matera, in southern Italy, has been designated as European Capital of Culture 2019 and is attracting an increasing number of tourists for historical itineraries in the old town. "Sassi", the old town of Matera, is a rupestrian settlement that Since 1993 have been included in the UNESCO World Heritage List with the following justification: "This is the most outstanding, intact example of troglodyte settlement in the Mediterranean region, perfectly adapted to its terrain and ecosystem. The first inhabited zone dates from the Palaeolithic, while later settlements illustrate a number of significant stages in human history". This UNESCO justification could be enriched by the unique geological attributes expressed by the area, that could become an urban geopark. The intimate connection of Matera with the geology is primarily suggested by the name Sassi indicating the rupestrian districts representing the old town: "sassi" is the italian word for stones, and the old town of Matera still conveys an idea of symbiosis with the original rocly landscape. The geographical background in which the Sassi districts developed is represented by the "Murgia Materana" (or "Murgia di Matera"), that is the rocky scenery in front of Matera spectacularly cut by the "Gravina di Matera", the canyon on which rigth side the old town is perched. Geologically speaking, the Murgia Materana is a wide rocky structural high corresponding to a paleoisland during early Quaternary times. Flanks of the paleoisland were mantled by a Quaternary calcarenite before to be cut by the "Gravina di Matera" canyon. There is no doubt that the "Gravina di Matera" is the element of the landscape that most characterizes the area; without the presence of this canyon and of two of its tributaries (the "graviglioni"), that now are the two main roads to enter in the Sassi districts, the rupestrian town could not have existed since the urban area of Sassi has been dug in the Quaternary calcarenite widely exposed along these rocky valleys.

Apart for proposing Sassi as an urban geopark, using simple and divulgative geological keys, tourists visiting the old town of Matera could appreciate an amazing geological tour being intrigued to understand the evolution of the crossed landscape.

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Keywords: karst processes, Middle Bussento Karst System, Cilento Geopark.

The Cilento, Vallo di Diano and Alburni National Park, founded in 1991, was the first Italian national park to be designed as Geopark in 2010 and as UNESCO Global Geopark in 2015. It spans from the Tyrrhenian borderland (where flysch units dominate) to the inner mountainous landscape (where carbonate rocks crop out). Its complex geological setting results in a large variety of stratigraphic and geomorphological features, whose scientific importance and scenery beauty are undisputed (Santangelo et al., 2005). In this paper, we propose two itineraries to discover the amazing and poorly known Middle Bussento Karst System, near Caselle in Pittari, SE of the Geopark. Itinerary 1 includes three stops representative of the overall geological setting of Caselle in Pittari and surroundings. It moves from the folded turbidites outcrop at the entrance of the village, up to the carbonate units of Mt. San Michele with its paleo- and neo-karst features and, finally, its sacred cave. From there, it is also possible to admire the southern part of the Geopark, encompassing the view of Mt. Bulgheria, Mt. Sacro, Mt. Centaurino and Mt. Cervati. The itinerary ends with a last stop close to terraced fluvial deposits, the unique uplifted fluvial deposit of the upper Bussento valley. Here, karren field slightly dissecting the carbonate rocks have been interpreted, for ages, as "devil footprints" by local people. Itinerary 2 is devoted to the discovery of the karst phenomena of the Bussento and Rio Bacuta rivers. It starts from the fascinating La Rupe Cave with its 30 m high cave portal where the Bussento stream sinks. It then includes three more stops in the amazing Caravo, Orsivacca and Bacuta ponor entrance, feeding groundwater discharge in the hypogenic karst cave system, that is progressively interconnected downstream with the Bussento river underground discharge. Groundwater discharge re-emerges 5 km to the S of Caselle in Pittari from the so-called "Bussento Resurgence", main touristic attractor of the Morigerati WWF Oasis and that represents the last stop of the second itinerary. Recent scientific interdisciplinary researches have studied the Middle Bussento Karst System as one of the most interesting karst system of southern Italy, spanning from the singular karst backflooding to the karst pulse floods, suggesting it as Experimental UNESCO Karst basin (Bovolin et al, 2017) for geodiversity conservation, protection and promotion. The itineraries can be appreciated by both simple visitors and geo-tourists, but also for scientific and educational purposes.

Santangelo, N., Santo, A., Guida, D., Lanzara, R. & Siervo, V. (2005): The geosites of the Cilento-Vallo di Diano national park (Campania region, southern Italy). Il Quaternario, 18(1), 101-112.

Bovolin, V., Cuomo, A. & Guida, D. (2017): Hydraulic modeling of flood pulse in the Middle Bussento Karst System (MBKS), UNESCO Cilento Global Geopark, southern Italy. Hydrological Processes, 31, 639-653.

## Session S38 History of geosciences and Geoethics: the right way for social responsibility

Conveners AND CHAIRPERSONS Marco Pantaloni (ISPRA, Roma) Silvia Peppoloni (INGV, Roma) Fabiana Console (ISPRA, Roma) Giuseppe Di Capua (INGV, Roma)

### Policy, economy and geosciences in the debate about Fucino and Trasimeno lakes (1780-1870 ca.)

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Keywords: history of science XVIII-XIX century, Trasimeno lake, Fucino lake.

Between 1780 and 1870 Fucino and Trasimeno lakes had been the involved in a heated debate concerning their future; at the end they had two different destinies: the first one has been dried up, the second has been preserved. The analysis of this debate is very interesting because it allows to verify and understand the relationship between economy, policy, geology and technological improvements (Lupi, 2014a; Lupi, 2014b; Alimenti & Lupi, 2016). The historical approach focuses the changes determined by political and institutional transformations from the late period of the Old Italian States, by the Age of Revolution, until the birth of Italian Kingdom. Therefore this research points out on the one hand the role played by geology in this huge challenges and, on the other, the links between scientists and power. Finally we can evaluate the social consequences of scientific and professional expertise on lakes.

The Authors examine the object considering many different historical sources: pamphlets, essays, political press and scientific magazines. So they can describe some topics especially connected to the economic interests of different social classes, the public health, the stature of the political approach and the output of the exchange between scientists and policy makers. At the end the Authors underline the relevance of the different conceptions - in space, time and social aspects - of 'public interest' (Alimenti & Lupi, 2017).

Alimenti, S. & Lupi, R. (2016): Un esperimento di interdisciplinarietà per le 'scienze politiche', in Ead. (a cura di), Ambiente e pubblica felicità tra idee e pratiche. Il caso del Lago Trasimeno, Franco Angeli, 7-14.

Alimenti, S. & Lupi, R. (2017): Il destino dei laghi. Il dibattito sul Fucino e sul Trasimeno (1780-1870 ca.), 77-111, il Mulino Bologna.

## The role of geological studies in large infrastructural projects in the 19<sup>th</sup> century - some examples from NW Italy

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Keywords: infrastructures, geological studies, 19th century.

Construction of large infrastructures like railways and roads has played a more and more fundamental role in economics and society development in the last two centuries. Since the middle 19th century, the Italian railway system has increased significantly; the expansion of the Kingdom of Italy was based on a large infrastructural plan that helped to remove the trade barriers across the different regions of the newly formed state and favored new international relationships (Ballatore, 2002).

The realization of that ambitious infrastructural project had to face the complex geological and geomorphological setting which characterizes the Italian territory, especially in mountain regions. Nonetheless, the importance of geological studies in choosing the most favorable paths and in guiding the technical choices was seldom acknowledged, as Federico Sacco polemically pointed out:"...I criteri geologici furono sovente tenuti in considerazione affatto secondaria od anche dimenticati del tutto...", wishing that "....nell'avvenire studi geologici accurati precedano sempre progetti tecnici e ne accompagnino l'esecuzione..." (Sacco, 1898).

In this contribution, we analyze the role of geological studies in the realization, in the 19th century, of large infrastructural projects through the Western Alps and the Northern Apennines, both characterized by a close juxtaposition of several tectonic units with different geotechnical characters.

In detail, this contribution will highlight the criticisms (made for example by Martino Baretti and Federico Sacco) to the path of the Torino-Bardonecchia railway crossing the Susa valley, where accurate geologic studies were performed in its upper part for the realization of the Fréjus tunnel (completed in the 1871 after two decades of works).

A second example will regard the region of Genova, where a complex infrastructural knot has been developed since the middle 19th century. Geological studies had a crucial role in steering the technical decisions, as demonstrated, for example, by the bitter controversy between Federico Sacco and Luigi Baldacci about the more convenient path to follow for the Genoa-Milano railway line (Sacco, 1908; Baldacci, 1909).

Baldacci, L. (1909): Sulle linee ferroviarie direttissime Firenze-Bologna e Genova-Milano. Boll. Soc. Geol. It., 28(1), 96-102.

Ballatore, L. (2002): Storia delle ferrovie in Piemonte, Punto Piemonte in Bancarella.

Sacco, F. (1908): Un allarme di Geologia applicata alle Direttissime Bologna-Firenze e Genova-Milano. Gior. Geol. Prat., 6(6), 148-155.

Sacco, F. (1898): La geologia e le linee ferroviarie in Piemonte. Tip. Gerbone.

# The geology between past and present: cultural heritage and the current social value of geosciences. The tragedy of the Rigopiano Hotel

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Keywords: Rigopiano Hotel, Geoethics, geologic hazards.

On the occasion of the scientific session on the theme "Geology in urban and territorial planning" organized by the Italian Geological Society and the Italian Section of the I.A.E.G. in Bari, October 10, 1975, the prof. Felice Ippolito in the opening speech, said:

... Il tema dell'odierna Seduta è dei più attuali: sarei inutilmente prolisso e superfluo segnatamente tenendo conto del gran numero di comunicazioni e relazioni attinenti al tema che dovremo ascoltare oggi.

... se volessi illustrare a voi qual è la funzione che la Geologia è chiamata a svolgere nella pianificazione urbana e territoriale.

... se volessi portare esempi, abbondanti e non edificanti dei guasti ambientali prodotti nel nostro paese e anche in altri (ancorché in misura minore) per il mancato preliminare indispensabile studio geologico nei problemi di pianificazione urbana e territoriale.

... se volessi elencare le cause che hanno creato nel nostro paese, in materia, una situazione di particolare disagio per l'ignoranza o la trascuratezza con cui le autorità competenti hanno preso in esame soluzioni progettuali, senza il necessario corredo di studi geologici preliminari...

The words pronounced by prof. Felice Ippolito are very up-to-date when we think about what happened on January 18, 2017 at the Rigopiano Hotel, in the municipality of Farindola.

The doubts that still persist today on the opportunity that the Rigopiano Hotel could be located in exactly that position give an idea of how geological knowledge is not yet the first discriminating factor in spatial planning.

This event materializes the EMPTINESS OF AWARENESS regarding the balances that control a complex system, i.e. "the natural environment", which welcomes us in spite of itself.

The geological knowledge of an area in its most authentic meaning is only that which is represented in space-time by a "historical perspective".

Finally, this concept has been reiterated also in the most recent legislation (NTC-2018) where the geological reference model of an area of interest defines the stratigraphic-structural setting of that area included in a wider geodynamic and morphodynamic context.

This paper aims to emphasize the importance of the vision of the geological research in professional practice where the rigor of the critical analysis of previous studies must be accompanied by the ability to recognize the objective stratigraphic, structural and geomorphological evidences, sufficient to assess the geologic hazards of a site.

The Rigopiano Hotel tragedy highlights how the concept of a significant volume of legislation can be misleading when applied to geotechnical aspects in just three sizes. We believe that the time variable must be hooked to the various geological processes to appropriately define the significant extension of the area of investigation that can not be resized on the basis of administrative boundaries or depending on the amount of the remunaration needed.

## The hypotheses of Jean Hoüel (1735-1813) on the formation of Etna. The evolutionary model of the volcano in the representation of the CXIX planche

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Keywords: Mt Etna, Jean Hoüel, volcanology.

During the eighteenth century there was a considerable interest in natural phenomena and in particular volcanic eruptions. This subject had become so common in painting that Pierre-Henri de Valenciennes dedicated in 1799 a specific paragraph of his Elements de perspective pratique à l'usage des artistes to the eruptions of the volcanoes (Abate & Branca, 2017). The indications on how to represent volcanic eruptions greatly influenced the graphic production of the innumerable traveling artists who chose Etna as the object of their representation. An exception in this sense is Jean Hoüel, painter and architect, who instead studies Etna as if it was an architectural monument to be measured and mapped. The author, in fact, provides geological sections of the volcano, tries to explain visually how a lava flow develops and produces views that perfectly agree with scientific observations. House is the author of the first stratigraphic sections of the eruptive vents of 1669 and of the earliest evolutionary geological scheme of Etna volcano. The contribution of the French artist to the volcanology of Etna of XVIII century is little known today although in the past his contemporaries had given some importance to his observations in this field (Abate & Branca, 2017). For example, in 1825 the famous geologist Leo von Buch in his Description physique des iles Canaries cited the studies of the French artist on Stromboli and in 1828 Hoüel's work appeared in the Volcans voice of the Encyclopedie Methodique together with the works of Kircher, Dolomieu, Ordinaire, Elie de Beaumont. In contrast, the scientific contribution of the French architect to the geology of volcanoes has been forgotten over time. In fact, already in 1838 the geologist Elie De Beaumont did not mention Hoüel in his work on the structure and evolution of Etna among the foreign travelers who had made the Sicilian volcano the object of their research. With this contribution we want to highlight an unprecedented portrait of the French architect who for the first time coincides with that of a modern volcanologist and scientific illustrator. In fact, Hoüel is the first author to translate the theories on the formation of Etna into images, focusing in particular the CXIX planche of his Voyage which illustrates for the first time the hypothesis on its formation and on the internal structure of the volcano.

Abate, T. & Branca, S. (2017): Jean Houel e la vulcanologia dell'Etna. In: Barbera P. & Vitale M.R. Eds., Architetti in viaggio. La Sicilia nello sguardo degli altri. 243-257. LetteraVentidue, Siracusa.

#### Sciences of Laws and Sciences of Processes for Earth Science

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Keywords: Science of laws, Sciences of processes, Deep Time.

Geologists, geophysicists and volcanologists have long drawn on historical and archaeological data concerning earthquakes, tsunamis, volcanic eruptions, landslides and floods. These are important data, which help scientists to gain further knowledge about natural events, their evolution, and their effects on the built environment. Such studies - in which "time" is the dimension informing investigations of the dynamics of extreme events and their impact on the environment - stand at intersections among different disciplines (Cubellis et al., 2017; Cubellis and Luongo, 2018).

For years, the disciplines of history and archaeology have invited questions such as: Do these disciplines engage in an autonomous critique of the phenomena they investigate? Is it possible to preserve the rigor and scope of research, even when its objectives are specific and limited? Or do we run the risk of staking out a research field that is subordinate to the typical investigation topics of Earth Science? How does this issue reflect on the quality of historical and archaeological research and on the scientific versant, and with what degree of awareness? Furthermore, long-term environmental-history topics are usually left out of current multidisciplinary investigations, while actually they could be the drivers of new investigations on the environment. Some very significant themes could be addressed, such as the slow transformation of landscapes as a result of human exploitation, climate variations and the reaction of human societies coeval with these variations, centuries-long ground deformation of volcanic areas and subsidence of alluvial plains due to anthropic action, and a history of superficial water resources and groundwater.

New multidisciplinary fields in history and archaeology could provide clues and content for new academic sectors. In Italy, planning capability in these sectors could develop even more if geologists, geophysicists, historians, archaeologists, architects and engineers intensified discussion between different disciplines on the languages, contents and perspectives that could emerge from this reflection. Case studies in this sphere should thus be carried out not only by those historians and archaeologists who for years have been devoting themselves to such finalized investigations, or by the Sciences of the Earth researchers who use the results of historical investigations, but also by historians, archaeologists, architects and engineers approaching the theme from other perspectives, who also wish to contribute their experience.

Cubellis, E., Luongo, G. & Obrizzo, F. (2017): Cultural climate in Naples between the birth and development of volcanology. Rend. Online Soc. Geol. It., Vol. 43 (2017), pp. 64-78, 6 figs., 10.3301/ROL.2017.36.

Cubellis, E. & Luongo, G. (2018): History of Ischian Earthquakes. Bibliopolis, Napoli, copyright 2017, pp. 138, plates XXVI.

### **Critique of Practical Geology**

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Keywords: Digital revolution, Practical Geology.

Digital revolution, economic and cultural globalisation, all together are bringing such radical changes in our modern society that the idea of a new anthropological revolution is spreading out, as big as the Neolitical and industrial ones. In the world of Practical Geology, where we live, we are experiencing all these changings which are developing with an uncontrollable speed. From a scientific point of view, geological sciences are reaching the highest level of accuracy thanks to new technologies, communication systems and data sharing. In the same way, from a "practical" point of view, information technology tools, have allowed the creation of quantitative geological models which are always more refined and similar to engineering. It is nowadays easy to "translate" into mathematics all the observations of nature; this is allowing the deterministic rendering of some holistic theories such as "Gaia Hypothesis" (Lovelock, 1979) which were considered more as a philosopy than as a science.

This process leads to an " iper specialization" of all these subjects, and as a result, the researcher and the practical man are not able any more of handling the whole work by their own, they need a complex synergistic organisation. A rusty complex burocratic machine has been created in order to manage this technocratic structure. As a result everythig is often dominated by legal, economic and monetary aspects as well as self-referential procedures which push aside the main technical aim.

Those who live in our world are catastrophically perceiving that this exaggerated technical scientific dynamism, even if leading to a future dominated by machines and artificial intellect, is risking to get stuck in the muds of "PIN" and "Password".

I have used the out if practice words "Practical Geology" to point out the inheritance that the Earth Sciences are handing out to the economic world in order to seprate it from the teaching of Technical Geology or Geo-Engineering. I ask the indulgence of the experts of Economics, Philosophy, History and Anthropology paraphrasing Nietzsche-to be like donkeys slipping on the polished floor of culture. I finally apologise to have wickedly stolen the title of my considerations from the great philosopher of Königsberg who, as a Physical Geography Professor, would probably have tenderly smiled (Kant I., 1802).

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### Paleontherapy - the new method in field of medical geology for the therapy of young disturbances

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Keywords: Paleontherapy, Rehabilitation, Teenagers.

The behavioral and psychological disturbances of kids and teenagers cover a very wide spectrum which comprises, for example, physical and psychic disabilities, psychological disturbance, real psychiatric derivations and various addictions and dependencies. Causes may be connected both to genetic or physiological contests, and to social and environmental habits in which guys live.

Practically, teenagers start to isolate themselves, closing progressively every way of communication with the external world. From Japan is the discovery of *Hikikomori* social pathology (Yong & Kaneko, 2016) which forces who is afflicted to imprison in the house, in a room together with his loneliness until, in some case, arriving to death.

Realized by Childhood-Teenager Mental Health (Salute Mentale Infanzia - Adolescenza - SMIA), at Italian National Health service (A.S.L.), some individual and/or group projects have been activated with the objective to stop or, more successfully contain the disturbance here discussed, trying to rescues and to permits a life as normal as possible.

Paleontherapy, one of said project, is realized by a joint ventures between operators of SMIA of Sesto Fiorentino (FI, Italy) and Cultural Association G.A.M.P.S. Scandicci (FI, Italy). The association manages an important mineralogical and paleontological collection exhibited in Badia a Settimo, Scandicci (FI, Italy).

The metaphor on which the project is based is that a fossil, before to be discovered, is as not existing. In this way, before to be discovered, a fossil doesn't speak about its history and together it cannot speak about the own world. When a fossil is found and is collected by rocks, it starts to tell about ancient and unknown worlds. On the same way, the guys followed by SMIA have something hidden inside and they must discover what and put outside to start to understand what the pain is and how to work with it. As paleontologists and geologists speak about environment, climate or everything using fossils, in the same way guys must speak about themselves and bring out their potentialities, in order to start to work on their disturbance.

Some positive feedbacks have been found, underlining enthusiasm and time investment that guys have done at exhibition of G.A.M.P.S.

Using fossils, the guys have started to tell and tell themselves, everyone following an own way, they have left themselves and have started to live situation out and far from their habits. They have started to use their time in a different way with a goal to reach and a program to follow, they have started to give themselves a challenge.

Actually the project is at the end on its first year of spin off, but several results are yet available, The spin off phase is useful to choice the better target to indicate for project, improvement of health objective, collection and transformation of feedback data. This project represents the first attempt to use Geology, and in this case, Paleontology for human health, on pathology, about youth people, with a very important social impact.

Yong, R. & Kaneko, Y. (2016): Hikikomori, a Phenomenon of Social Withdrawal and Isolation in Young Adults Marked by an Anomic Response to Coping Difficulties: A Qualitative Study Exploring Individual Experiences from First- and Second-Person Perspectives. Open Journal of Preventive Medicine, 6, 1-20.

### Marcello Carapezza (1925-1987), Scientist and Humanist

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Keywords: Marcello Carapezza, geochemistry of fluids, volcanic surveillance.

In the year 1970 Marcello Carapezza (1925-1987), returned to the University of Palermo as full professor in Applied Geochemistry after ten years of absence. His arrival would have marked a turning point in studies of Earth Sciences at the University of Palermo: today we remember Professor Carapezza to the younger generations, so that they can keep his memory.

Graduated in Chemistry, Carapezza began his university career in 1948 as assistant professor of Mineralogy. Shortly after, his interests were extended to Earth Sciences. Carapezza was immediately distinguished for its ability to establish inter-university collaborations and to catch innovative ideas, in full harmony with the great transformations of the Geosciences at that time. These openings led him to move from Palermo to Bologna in the late 1950s; but, before that, he had an intense period of research in Experimental Petrology at the College of Earth & Mineral Sciences of Pensylvania State University (USA), where a group of scholars, who have made the history of Petrography, such as E.F. Osborn, J.W. Greig, P. Wyllie, G. Ulmer, was active.

After returning to the University of Palermo in 1970, professor Carapezza gave a new direction to his research, experimenting in the volcanic areas surveillance that would be established years later. He opened a new field of study in Italian science: the geochemistry of fluids applied to natural systems. The success of these studies, developed together with a new group of researchers that he formed, gave birth in 1980 in Palermo to the Istituto di Geochimica dei Fluidi (IGF), of which Carapezza was director until his premature death, in 1987 IGF continued to operate until 2001, when it was incorporated into the Istituto Nazionale di Geofisica e Vulcanologia (INGV), becoming the Palermo branch of this institution. The IGF, since its foundation, carried out a systematic geochemical control of the activity of both the Sicilian volcanoes and the Phlegraean Fields, becoming the model and the forerunner of modern automatic monitoring centers for active volcanoes.

The focus on Marcello Carapezza scientist must not overshadow other aspects of his rich personality: the refined taste for letters, love for music and the arts, attention to the archaeological, architectural and environmental heritage. To this sphere of interests belong some works of Carapezza and collaborators who represent brilliant applications of geochemistry to the study of cultural heritage.

In the '80s Marcello Carapezza, then Vice-Rector of the Palermo University, proposed that the historic Palazzo Steri in Piazza Marina, should become the seat of the Rectorate, the first nucleus of the rebirth of an area of the historic city center then severely degraded. The lavish commitment to the restoration of Steri and the sense of redemption that Marcello Carapezza was able to give to this initiative were decisive in convincing Renato Guttuso to donate to the University the large painting Vucciria, which is now exhibited in the Sala dei Baroni.

As a tribute to this passionate scientific and civil commitment, the University of Palermo has dedicated the hall of Palazzo Steri, in which the meetings of the Academic Senate are held, to the name of Marcello Carapezza.

## The research of the western Tauern window between 1894 and 1898 in the documents of the mineralogist and petrographer Friedrich Becke. A project of the "Österreichische Akademie der Wissenschaften"

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Keywords: Friedrich Becke's notebooks, western Tauern window.

Friedrich Becke's notebooks are witnesses of his remarkable and multifaceted scientific oeuvre. Geoscience owes the following discoveries to Friedrich Becke: the theoretical knowledge about crystal classes, the further development of the research regarding feldspars, the technical development of microscopes, and the geological investigation of the Waldviertel, the Sudeten and the Alps. His most significant discovery was the "Becke Line". The notebooks provide evidence for the mineralogical, petrological and geological techniques used during the late 19<sup>th</sup> century.

Becke's notices about his fieldtrips in the Alps are generated in between twenty years, between 1892 and 1912 and are documented in different styles as notebooks, field books and laboratory books. Between 1893 and 1903 he filled 18 field books and three notebooks containing his research in the Eastern Alps. Together with the geographer Ferdinand Loewl (1856-1908) he examines the rocks and geological formations of the Southern Alps of Predazzo and the geological structure of the Zillertal Alps.

Between 1894 and 1898 the Commission of the Academy of Sciences approved a petrographic study of the Zentralkette of the Eastern Alps. Three regions were explored by three scientists - Friedrich Martin Berwerth (1850-1918), Johann Ulrich Grubenmann (1850-1924) and Friedrich Becke. Friedrich Becke conducted research in the eastern and western Tauern Window. The documentation describes his visits in the area of the Zillertal and the Tux Hauptkamm with further studies in the Brenner area extending over 10 years between 1893 and 1903. His active participation in the 9th Geological Congress in Vienna can be seen as a research highlight and also as completing the work in the Zillertal and the Tux Alps. The petrographic laboratory studies of the rocks of the Zillertal Alps lead Becke to fundamental discoveries in the field of crystalline schists and metamorphic rocks.

These two areas of research - Zillertal and Tuxer Alpen respectively Hochalm Massiv - have established the Tauern Window in the Alps and given it a firm place in Alpine geology. With his petrographic research and the resulting findings, Becke sets the basis for future discussions of this interesting area.

## Well construction and underground fluids in pre-industrial ages: Scientific observations, ethical speculation and medical contributions of Bernardino Ramazzini on the health and safety of *Putearii* (water well diggers)

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Keywords: Bernardino Ramazzini, Occupational diseases, Water well construction.

The Italian scientist and physician Bernardino Ramazzini (1633-1714) is well known in the field of geosciences for his observations concerning the occurrence of underground water and the interpretation of the origin of artesian pressure (1691, De fontium mutinensium admiranda scaturigine, On the admirable water springs of Modena). He did not coined nor used the expression "artesian", a term that prevailed only in the beginning of the XIX century in France, where many "artesian" wells were being drilled in the region of Artois. Ramazzini constructed a physical model of this phenomenon, which he attributes to the principle of communicating vessels, using it to repeat the pressure measurements with a Torricelli barometer. Ramazzini extended his scientific interests also to several geologic and stratigraphic issues, and published the first hydrogeological cross-section known in the literature, which highlights the relationship between the different hydrogeological complexes. He also anticipated the studies on atmospheric electricity, the nature of oxygen and ozone, and investigated the natural history of the well-known seepages of crude oil in the province of Modena (Montegibbio and Montefestino). At the time, this valuable *olio di sasso (oleum petrae, i.e., petroleum)* was actively produced from hand-dug wells or skimmed from natural seepages. Ramazzini also tried to measure water temperature and air pressure in water wells with the barometer and the thermometer used in medicine, and he published, first in the world, many charts of water temperatures up to a depth of 20 m (Ephemerides barometricae, 1695, Barometric ephemeris). In 1690, G.W. von Leibniz visited Modena and spent many days with Ramazzini, appreciating his works and his scientific methodology. In 1700 Ramazzini published his masterpiece *De morbis artificum diatriba* (On the diseases of workers), which remained, for more than two centuries, the main reference for the epidemiological study of occupational diseases, and which was translated into many languages. Following the teaching of Hippocrates, he coined the motto longe praestantius est praeservare quam curare (prevention is better than cure). Of great interest, also from the technological standpoint, is the chapter on the health of water well diggers (*Putearii*). Ramazzini is interested in observing his patients on the job, convinced that he could better identify the etiology and pathogenesis of their diseases. Ever more convinced that his patients' conditions are attributed to environmental situations, he addresses observation to the characteristics and conditions of the environment in which they operate. The study review the technology of well construction up to the mid-XVIII Century, explore the contribution of Ramazzini in the field of hydrogeology and his descriptions of the drilling techniques developed by the water well diggers of Modena, together with their occupational diseases.

## The "rebirth" of the Torbidone River (Norcia Plain, Umbria): a historic and geoethic approach

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Keywords: History of geology, hydrogeology, Umbria.

In the Norcia Plain (Umbria, Italy), the Torbidone springs are characterized by periodical vanishing and reappearing, flowing in its natural riverbed.

The intermittent character of these springs has always intrigued people who, for centuries, entrusted the belief of a seven-year periodicity of the cycle of these springs. The hydrogeological characters of these springs are under study, because of their peculiar features (Petitta et alii, 2018).

Many authors described the wonder of these springs and their periodically appearance. The first citations was in the *Dittamondo* wrote by Fazio degli Uberti (1345 ca.), that spoke about the seven years periodicity of the springs. Since then, many authors deal with this argument, both from a scientific or juridical point of view (Console et alii, 2017).

Bartolo da Sassoferrato in 1576 in his treatise *Tyberiadis* dealt with the issue of the legal regime of rivers and their riverbed, introducing the concept of abandoned bed.

In the treatise *De fluminibus*, Giovanni Francesco Ripa (1575) described the conditions under which a riverbed could be changed, using the Torbidone as example: "Quod si flumen solitus sit reverti, non dicitur mutatus alveus, exemplum in flumine defluente per territorium civitatis Nursiae, quod Turbido nuncupatur, quos a mille annis solet septennio fluere et septennio se abscondere".

The seven-year periodicity of the Torbidone springs spread in popular opinion at least until 1859, in the immediate aftermath of the Norcia earthquake, accurately described by Angelo Secchi.

The last disappearing of the springs was in 1979, immediately after the Valnerina earthquake. Following the 2016 Central Italy earthquake, the springs reactivated after the 3<sup>rd</sup> shock (Mw=6.5), shows a gradual increase in flow rate from 0 up to 1.5 m<sup>3</sup>/s in about 3 months.

During the period 1979-2016 the riverbed of the Torbidone has been man-made for agricultural and infrastructural purposes. Immediately after the spring reactivation, and the high water flow rate, it was necessary to quickly reshape the original fluvial bed to avoid the flooding of a large area. This case study shows how anthropisation processes often neglect and do not take into account the natural phenomena that persist in a specific territory.

The urgent realization of hydraulic work to regulate the Torbidone stream, whose waters flooded the Norcia plain, highlighted the need to respect the natural dynamics as the first, fundamental action to mitigate the hydrogeological risk.

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## The social value of geological knowledge in the supernatural narratives of the ancient world: some case studies

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Keywords: Geoethics, geosciences, social sciences.

The concept of Geoethics involves not only the responsible behaviour of professionals and researchers in geosciences, but also the societal and cultural relevance of geosciences. The interaction between geosciences, social sciences, and humanities helps to strengthen the relationship between communities and the land they inhabit and contributes in creating a shared space for the cultural and social aspects of geosciences (Peppoloni et al., 2017).

In this regard, the memories of past geological events encoded in mythological and legendary narratives may provide valuable insights to social sciences and shed new light on the early human perception of the world. Conversely, the latent geological information in a myth could contribute to our geological knowledge. This mutual interaction may (i) provide missing elements to the historical reconstruction of ancient sites, (ii) supply important data to evaluate natural hazards, and (iii) enhance the relevance of geological issues as primary cultural assets.

For instance, many ancient Sanctuaries were built on active faults, due to the unusual phenomena witnessed on these sites (Piccardi, 2001). One of the most representative is the Oracle of Apollo at Delphi. The fulcrum of the oracle, the principal oracular centre in the Aegean world for almost two thousand years, was a natural gas-emitting chasm in the rocks. At present, no gases are released and no open cracks are present in this archaeological site, but a seismic fault can be identified in the area, which has been reactivated in historical times (373 BC, 1870). Therefore the mythological chasm can be traced back to a past rupture of this seismic fault (e.g. Piccardi, 2000). Such a reconstruction contributes to both analysing natural hazards and understanding the origin of the Oracle. In addition, the fault itself is a primary touristic attraction.

Another example is the Mefite d'Ansanto, a small lake near Avellino where concentrated  $CO_2$ -H<sub>2</sub>S gases emanate, which are lethal if inhaled. Since the 6<sup>th</sup> century BC this area has been the main Sanctuary of the underworld goddess Mefitis (hence the name of the geological phenomena "mefites") for the Samnites and the Romans, regarded as a gate to the lower-world (e.g. Aeneid, 6). The gases rise through a seismic fault beneath the mefites, and a strong increase of this activity was observed during a seismic crisis in the 18<sup>th</sup> century and the night before the Irpinia earthquake of 1980 (M 6.9).

The Lake Averno, a crater lake emitting sulphurous vapours in the Phlegraean Fields volcanic region near Naples, was regarded as a passageway to hades: sacred to the infernal goddesses Hecate, Demeter and Persephone in classical time (Odyssey, 11; Aeneid, 6), and considered the door from which Christ descended into hell in Medieval tradition. In 1538 a tangible connection with the underground at this place was shown by a spectacular eruption that built in a week a 140 m high volcanic cone (Monte Nuovo), just at the site of *"Porta Christi"*.

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# Inventor, Engineer and Earth Scientist in a single brushstroke: Leonardo da Vinci and the earliest conception of sustainable land management on a constantly changing Planet

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Keywords: Leonardo da Vinci, Geoethics, land management.

Italy is a geologically 'young' country, where several natural processes related to tectonics, earthquakes, landslides, and evolution of the landscape are still very active and often dramatically energetic. Recognizing the natural hazards linked to this complex geological framework, the scientific and social role of the Earth Scientist in Italy is crucial and of primary importance, also on an ethical level. Geologists have a deep understanding of natural processes, their products, and evolution over time; knowledge which is critical to plan sustainable coexistence between human activity and natural phenomena. This contribution demonstrates that earliest understanding of the importance of developing land management practices in line with natural phenomena and human activities can be traced back to the genius of Leonardo da Vinci, as early as the sixteenth century. In a cultural scenario when natural science studies were caged within the dictates of Biblical fixism and the 'indisputable' authority of classical authors, Leonardo stands out for his freedom of thought, and deep understanding of the principles of Earth Science; complex aspects that will be fully understood only three centuries after the work of the great scientist and artist. Leonardo's deep understanding of natural science led to recognition of the need to reconcile the planning of human activities (in particular engineering works) with the constantly changing surface of the Earth. Leonardo not only made actualistic observations and undertook experiments to interpret processes and products of the geological past, but also used his deep understanding of past geological processes to make 'visionary' predictions on the future evolution of our changing planet.

#### The Expanding Earth: a disproved scientific hypothesis surviving its falsification

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Keywords: Geodynamics, pseudoscience, expanding Earth.

During the first half of XX Century, the idea that the planet Earth had expanded its volume through time enjoyed some success among the Earth scientists, but rapidly lost ground against Plate Tectonics. However, the idea was never completely abandoned (Sudiro, 2014; Edwards, 2016). More recently, Shen et al., (2011, 2015) and Edwards (2016) claimed that geodetic data do support slow planetary inflation. Actually, extrapolating back in time the expansion rates of Shen et al. (2011, 2015) and Edwards (2016), the resulting variation of the Earth size falls close to the values that Ward (1963), McElhinny (1978) and Wu et al. (2011) considered not significant to prove any change in the radius of the Earth. These results are also significantly smaller than the expansionist estimates of dwarf Earth radius. Therefore, against their own conclusions, also the calculations of Shen et al. (2011, 2015) and Edwards (2016) disprove any evidence of Earth expansion.

A century ago geologists could experiment with different geodynamic models because of the lack of constrains due to the limited data available, but a modern theory has to integrate the wealth of knowledge accumulated in geology and many other branches of science, drastically narrowing the range of scientific speculation. Therefore, in order to keep their hypothesis alive, modern expansionists must accurately pick only the data validating their ideas while rejecting or neglecting any contrary evidence.

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# The role of the institutions for the birth of the professional geologist between the 18th and the 20th century

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Keywords: history of geology, geological institutions, geoethics.

The aim of this paper is to investigate and reconstruct the establishment of a new scientific professional figure devoted to the study of the features and the history of the Earth from the late 18th century until the early 20th century.

Within the process of the disciplinary definition of geology as a science, the role of the geologist was also gradually outlined, not only concerning the aim of his work and the objects of his research, but also in relation to his teaching and social tasks, with inevitable ethical implications.

The early traces of the emergence of a new figure of 'specialized' geologist may be found in particular within the activities of institutions such as scientific academies and societies, as well as mining academies and schools in the late 18th century: but it will be better identified in the geological surveys, geological societies and universities during the 19th century, as well as in other state bodies and research centers established in the following century. The geologist will also have a significant role in the development of a new concept of natural environment between the late 19th century and the early 20th century (particularly in France and Italy) through the growing of a new literature of popular science, which significantly reached a great number of readers, also creating a new audience for naturalistic subjects related to the history of the Earth and its landscape.

This process of professionalization will be analyzed through some significant historical cases, in order to contribute to the definition of the origins and the early development of the ethical involvement of the geologist in the society.

# **Session S39**

Fifty years after the Belice's Earthquake. Considerations on geological, geophysical, geochemical, territorial and social aspects of this earthquake and its heritage in the connections between the Italian society and seismic catastrophes

> Conveners AND CHAIRPERSONS Mario Mattia (INGV, Catania) Paolo Madonia (INGV, Palermo) Giulio Selvaggi (INGV, Roma) Giulia De Spuches (Università di Palermo) Francesco Martinico (Università di Catania)

# The 1968 earthquakes and the ghost towns in the Belice valley (western Sicily): a stage of the virtual seismic itinerary through Italy

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Keywords: 1968 earthquakes, ghost towns, Belice valley.

Destructive earthquakes leave traces not only on the physical landscape (fault scarps, landslides etc.) but also human processes. Among the most devastating consequences there is the abandoning of settlements, even important ones, in favour of locations deemed safer. Abandoning a village and resettling in a new location, whether it is a gradual process or as a result of a sudden traumatic situation, represents an event with great historical, cultural and anthropological impact. It entails the loss of a piece of history or culture - local identity - and the more suddenly it happens, the more dramatic the after-effects.

Italy has almost two hundred localities recognised to have been abandoned for different causes (landslides, floods, volcanic eruptions, but also social or environmental reasons), some ninety of them in consequence of earthquakes. The abandoned settlements are thus the most spectacular attestation to the fragility of the land. Sicily, land of volcanoes and earthquakes, has several archaeological traces of the old villages either in the form of fairly substantial ruins, or of half-destroyed villages, which are usually located only a few kilometres away from the new settlements. The rediscovery of the ghost towns represents not only a tool for earthquake education strategies but also an important moment of cultural growth. At a local scale, each ghost town is a veritable "place of memory", that contains the perfect synthesis of the impact of earthquakes on history, architecture and social dynamics.

In this paper we present the methodological approach developed in the framework of the EDURISK Project (Earthquake eDUcation: a journey for seismic RISK reduction) to enhance the awareness of seismic risk as an element of daily life. The materials used to this aim are very different: documents on the history of each abandoned settlement, iconographic materials showing their evolution over time up to the present state, historical documents on the effects of the earthquakes and the choices and complex process of reconstruction. The case-study of the Belice valley and 1968 earthquakes well represents the richness and complexity of this approach, including also newspapers and television reports.

Following this rationale, we have published in 2006 the first multimedia devoted to Sicily based on the tools available at that time: a DVD-Room hosting the interactive technique Quick Time<sup>TM</sup> Virtual Reality format (QTVR). Today multimedia technology is much more advanced and web-oriented, and facilitates the developing of new itineraries through the seismic history of Italy, but the methodological approach is still valid.

# A reappraisal of the 1968 Belice valley seismic sequence: a case study of intensity assessment with cumulated damage effects

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Keywords: 1968 earthquakes, macroseismic data, Belice.

In 1968 six shocks with magnitudes between 5.2 and 6.4 destroyed or heavily damaged several towns in the Belice Valley (western Sicily), causing some three hundred fatalities. Seismologists and geologists provided first reports on field observations mainly on macroseismic features (De Panfilis & Marcelli, 1968; Bosi et al., 1973). Later, Barbano et al. (1980) and Cosentino & Mulone (1985) carried out a-posteriori studies aimed at detailing main and minor shocks; more recently, Guidoboni et al. (2018) produced further analyses based on previous studies and archives' material, newspapers and magazines.

However, these studies show some discrepancies in intensity assessment, since the MCS scale was used as an estimation of shaking rather than a representation of the damage scenario at a given locality. We think that it is a nonsense to assign an intensity 9 after a destructive shock and then 7 for a minor aftershock. The recent survey of the 2016-17 seismic sequence in Central Italy proved the difficulty to estimate macroseismic intensities in localities repeatedly hit by strong shocks and consequently to derive macroseismic parameters (epicentre, magnitude), which result inconsistent with the instrumental locations.

For the 1968 shocks, the catalogue CPTI15 (Rovida et al., 2016) reports macroseismic epicentres, though aware of the bias in locations. Available instrumental data appear poorly constrained, since the inadequacy of the seismic network operating in the late 1960s; only magnitude values may be considered reliable.

Here we propose a reappraisal of the 1968 Belice earthquakes following a methodology tested during the 2016-17 seismic sequence in Central Italy. We re-analyse primary sources, including newspapers and archive documents, to reconstruct the evolution of damage scenario during the sequence and, finally, to assess intensity by using the European Macroseismic Scale.

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# Morphotectonic evolution of the area affected by the 1968 Belice earthquake sequence, Southern Italy

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Keywords: Morphotectonics, uplifting, marine terraces.

The results of a morphotectonic study carried out in the area affected by the 1968 Belice earthquake sequence are shown. The investigated area is located in the southern part of Western Sicily; it consists of a southern coastal side characterized by large plains distributed at different altitudes, and of a northern inland side marked by deep valleys isolating small rounded hills or higher mountains. The geological setting is characterized by Tortonian to Lower Pleistocene terrigenous clastics and evaporites representing the fill of a foredeep basin evolving to wedge-top basins; these deposits cover a south-verging thrust system that is made by Permian to Miocene deformed carbonate rocks belonging to the Sicanian and Saccense successions (Catalano et al., 2013; ISPRA, 2013 and references therein). The geomorphological setting is marked by a stair-step flight of Lower to Upper Pleistocene uplifted marine terraces developing from sea level up to about 450 m a.s.l., in the southern coastal side; and by a dense network of deep river valleys isolating small rounded hills or steep and large structural mountains coincident with tectonic highs (pop-up or anticline-type mountains), in the northern inland side. The flanks of the structural mountains are wide fault scarps or large fault-line scarps and inclined structural surfaces. The collected data point out landforms produced by a downward migration of erosion, indicating a gradual lowering trend in the general base level of erosion due to tectonic uplift (Di Maggio et al., 2017). Causes of tectonic uplift (0.3-0.4 m/ky) are the constant southward migration of the thrust system and its foredeep (Monaco et al., 1996), and the following elastic rebound of the slab, resulting in the progressive southward shift of the shoreline and in the upward and inwards gradual moving of the new relief above sea level.

#### Archaeoseismological evidence of earthquakes Atselinunte: a review

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Keywords: archaeoseismological analysis, archaeological ruins, earthquakes dating.

Selinunte, a Greek colony located in SW Sicily, is the largest archaeological park in southern Italy hosting well-known classical temples showing evidence of possible earthquake damage. The temples were built in three different sectors: the Western Hill, named also La Gaggera, the Acropolis, and the Eastern Hill. In recent years, a detailed investigation has been performed at Selinunte aimed at reviewing all the archaeological data on the ancient earthquakes in order to improve the known chronological intervals. Furthermore, the survey was aimed at identifying additional evidence of seismic damage in between the archaeological ruins of the park..

This research was focused on the review of all the published data, and the identification of new undocumented evidence either in the same archaeological area of Selinunte or in the nearby sites through a territorial approach. To this aim, an in-depth bibliographic research was carried out to review all the recently published data as well as data coming from recent archaeological excavations. The data show that the archaeological area at Selinunte was destroyed at least by two violent earthquakes in Antiquity. The earlier one occurred in between 370 and 300 BCE, evidence of which has been documented for the Western Hill, and more recently in the Temple R located on the Acropolis of Selinunte, next to the Temple C.

During new excavations, archaeologists documented evidence of this earlier seismic event in the Temple R, in particular, they found the building completely collapsed on the ground. The remains of the outer walls appear deformed and tilted, opened joints among the wall blocks are still visible. Most of the wall blocks are completely fractured, although the fractures end within the same block. Other evidences are relative to blocks corners that appear broken. From the archaeological stratigraphy results that this building undertook a phase of reconstruction and restyling before 300 BCE.

The younger event instead has a larger time bracket between 330 and 500 CE. This event was more devastating than the previous one, erasing to the ground the entire ancient city (Acropolis and Eastern Hill). It produced the collapse of all the temples of the Acropolis (A, B, C, D, and O) and those located in the Eastern Hill (E, F, and G). Another evidence possibly associated to this event is the reconstruction of a statio (stop station) located at Sciacca (few km away from Selinunte). An inscription, today lost, mentions the reconstruction of a statio identified as Thermae Selinuntiae around the middle of the 4th century CE. If the reconstruction of the Thermae Selinuntiae was caused by a seismic event, we could hypothesize that the second seismic event took place some years before the reconstruction, and thus reduces the time bracket at between 330 and 350 CE.

# A new dataset of geodetic and InSAR data for the detection of active faulting in southwestern Sicily

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Keywords: Belice earthquake, Geodesy, GNSS data.

We present the first results of the analysis of geodetic and InSAR data collected in a project financed by the "Struttura Terremoti" of INGV to investigate the potential sources of earthquakes in south-western Sicily, including the area hit by the 1968 Belice earthquake sequence and the archaeological area of Selinunte, affected by two earthquakes in historical times. We adopt a multi-disciplinary approach, with the goal of addressing the following points: 1) define the active tectonic framework of south-western Sicily, 2) investigate and characterize on-shore potential sources of damaging earthquakes, and 3) evaluate the current deformation rates. To do this, we collected a new set of GNSS data from permanent remote stations and GPS data from permanent and episodically surveyed station in SW Sicily with a twofold aim: 1) to retrieve new insights about the geodynamics of this sector of Sicily and 2) to verify the active deformation of the creeping segment already identified by Barreca et al. (2014) between Campobello and Castelvetrano. We re-surveyed the IGM (Istituto Geografico Militare) benchmarks of this area and a new set of benchmarks already measured in 2007 by the University of Palermo for cartographic applications. Finally, we performed the SENTINEL 1A-1B Advanced DinSAR analysis covering the 2014-2018 time spanning, in order to investigate the recent dynamics of the structural lineaments located in the Campobello-Castelvetrano area.

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#### Relationships between soil CO, flux and tectonics structures in SW Sicily

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Keywords: soil CO, flux, active tectonic structures.

The identification and characterization of seismogenic structures in western Sicily is an open problem both for the geological-structural complexity of this sector and scarce seismicity. In addition, several zones are characterized by no clear morphological evidence of fault structures. To investigate the position and geometry of hidden active faults, besides geophysical methods also the study of areal distribution of soil  $CO_2$  flux is a valid methodology. Indeed, active tectonic structures are channels with high permeability through which the deep fluids (mantle and crustal) can easily reach the atmosphere. Follow that the alignment of high degassing area can reveal the presence of preferential ways of rising fluids i.e. faults.

We applied this methodology in SW Sicily in the surrounding of the area hit by the 1968 seismic sequence and the areas where major energetic seismic events (M>3.0) occurred during the last 30 years. We conducted several measurement campaigns of soil CO<sub>2</sub> flux and to obtain information on the origin of the gases, we also determined the isotopic composition of the carbon of the CO<sub>2</sub> in several soil gas samples.

A first measurement campaign was carried out in the NE portion of the Belice valley, near the artificial basin of the Garcia dam, the measures were carried out along the only known active deformation zone in this sector, the range of measured values falls within the range of variability typical of  $CO_2$  flux of organic origin. The highest values, however, were recorded close the active deformation zone. A second wider investigate area is placed in the NE part of the Belice Valley, the measurement points were homogeneously distributed around the syncline of the Belice. The range of soil  $CO_2$  flux measured is very wide and the highest flux values are definitely higher than those of organic origin. The map of the spatial distribution of the soil  $CO_2$  flux clearly shows as the high degassing areas are mainly aligned along SW-NE direction. This alignment orientation coincides with the orientation of the main tectonic structures recognized in the area.

A third measurement campaign was carried out S of Castelvetrano in an area of intense active deformation with evidence of a reverse fault with a SSW- NNE trend cutting an ancient settlement. About 30 soil  $CO_2$  flux measurements were carried out, distributed mainly around the ancient settlement. The distribution of soil  $CO_2$  flux appears to be quite homogeneous and almost all the measured values falls within the range of organic soil  $CO_2$  however carbon isotopic composition reveled the presence of deep origin component. Finally, a measurements campaign was conducted in area of Santa Ninfa gypsum karst structure, in particular along a transect above the caves. Interesting the soil  $CO_2$  flux values were among the highest measured.

## Active Geodynamics of the Central Mediterranean Sea: mantle-derived helium evidences in western Sicily

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Keywords: Helium, fluids, transfer tectonic.

The geodynamics of the Central Mediterranean is characterized by the interaction of the European plate with the African one. In this region, the Apennine-Maghrebide accretionary prism is made up of carbonate platforms and connects two areas affected by extensional tectonics: the subduction-related back arc basin Tyrrhenian Sea to the north, and the Sicily Channel to the south-west. Since the Trias a continental rifting has affected this region, and has produced extensive and trans-extensive system faults, which have a N-S orientation. Alkali-basaltic rocks have been found inside the sedimentary sequences of this age, indicating that these system faults were connected to the mantle. Since the Oligocene the opening of the Ligure-Provenzale basin and the rotation of the Sardo-Corso block has induced a change in the tectonic regime of the area. The thrust systems forming the prism were affected by right-lateral trans-pression between the latest Miocene and the Pliocene, while the rifting was particularly intense from Pliocene to late Quaternary.

Three main thermal systems have been identified in the orogenic belt of western Sicily. We looked at geochemistry as being a possible tool to be used to obtain a better understanding of the tectonic and geodynamic processes at work in the area. In this respect, helium is a powerful geochemical tool as its isotopic composition appears to be correlated with geotectonics. In fact, mantle-derived helium distributions in continents characterize areas undergoing extension or regions with contemporary basalt additions. Conversely, radiogenic helium produced in the crust and marks stable continental areas and/or continental margins and accretionary prisms, through which the forces deforming the rocks are able to squeeze out fluids accumulated in the crust. In turn, these fluids are channelled up through discontinuities and faults.

We report results on both the estimated excess of heat flows and the high <sup>3</sup>He/<sup>4</sup>He isotope signature in western Sicily. The estimated mantle-derived helium fluxes in the investigated areas are up to 2-3 orders of magnitude greater than those of a stable continental area. Furthermore, the heat flows reported in literature, are also greater than those estimated on the basis of the crustal radiogenic heat and the conductive mantle contribution. Our results indicate magma accumulation below the continental crust of western Sicilian and out-gassing of the same through roughly N-S trending lithospheric faults that have an extensional component. Although the identification of these faults is not sufficiently constrained by our data, they could probably be linked to the pre-existing faults that originated during the extensional-transtensional tectonic phases of the Trias-lower Oligocene or to the western Sicily wrench zone, which extends from the Tyrrhenian Sea towards the main rift system of the Sicily Channel.

# From Belice to nowadays: preliminary comparative analysis of multiple parameters describing seismic disasters

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Keywords: seismic disaster, societal impact.

One of the challenges on understanding disasters is a global approach to their scenario of injuries, deaths, homeless and economic losses. Analysis of disasters is more often fragmented into detailed investigations of specific aspects, underestimating the potential of having a more general perspective. Seismic disasters for instance are not just the results of the energy released by the earthquake or the vulnerability of buildings, but evidences that social, demographic, cultural parameters may play a crucial role.

A disaster is defined as "a serious disruption of the functioning of a community or a society at any scale due to hazardous events interacting with conditions of exposure, vulnerability and capacity, leading to one or more of the following: human, material, economic and environmental losses and impacts." (UNISDR definition of "disaster"). According to this statement, we intend to collect and put together some of the parameters that can characterize disasters caused by main earthquakes occurred in Italy in the last fifty years. Parameters that will be taken into account will range from seismic (i.e. Magnitude, depth, day and time, epicentral area, I-MCS) to geologic, geographic, demographic items, as well as the historical seismicity. Moreover, they will include government countermeasures that were taken after major disasters. The objective is to give a contribution to build a database of multiple parameters for a comparative analysis along a timeline, starting from the Belice zero-event till today to understand their relationship and their societal impact.

# Chemical and isotopic signature of groundwater in the Santa Ninfa karst system: possible relationships with neotectonic activity

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Keywords: Geochemistry, Neotectonic, Santa Ninfa.

The karst system of Santa Ninfa, hosted in a Messinian gypsum monocline (Agnesi & Macaluso, 1989), dipping south-eastwards, is located in the hearth of the area struck by the 1968 seismic sequence of the Belice valley. A dense network of karst discontinuities drains underground meteoric water, recharging an aquifer that feeds several little springs, located along both the southern and northern boundaries of the gypsum monocline (Favara et al., 2001). The main flow direction of groundwater is southward, controlled by the regional topographic slope and the general structural layout of the area. From the geochemical point of view, the Langelier-Ludwig classification diagram highlights the presence of two end-members: one related to water circulating in carbonate-dominated rocks and another one constituted of sulphate-rich groundwater; in between, a series of springs show a variable mixing between these. Binary diagrams, where concentrations of pairs of ions are plotted, evidence the dissolution of primary minerals and re-precipitation of newly formed ones. From the isotopic point of view, values plotted in a dD/d<sup>18</sup>O diagram show a positive shift for oxygen, highlighting the occurrence of evaporation processes during the hydrogeological cycle. Due to their composite chemical nature, these aquifers could react to stress field variations with geochemical anomalies driven by relative permeability changes, as already observed for the thermal spring of Acqua Pia during the 1968 seismic sequence (Favara et al., 2000).

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#### The active thrust front in south-western Sicily: hints on the Belice and Selinunte seismogenic sources

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Keywords: Active thrust system, southwestern Sicily, historical earthquakes.

We present an updated seismotectonic model of the active thrust front in southwestern Sicily, which encompasses the area hit by the 1968 Belice earthquake sequence and by the destructive historical earthquakes recorded by Selinunte temples and that was included in the latest release of the DISS database (<u>http://diss.rm.ingv.it/diss/</u>). The active *South-WEstern Sicilian Thrust* (SWEST) is formed by two non-parallel arrays, the *Mazara-Belice* (MB) in the north and the *Castelvetrano-Capo Granitola* (CCG).

Integration of geologic and geomorphologic data indicates that each structural array is composed of few distinct segments, each of them representing the south- or southeast-dipping forelimb of a broad fold. In turn, these folds are the uppermost expression of steep crustal ramps (Monaco et al., 1996; Meccariello, 2018) which upthrust the Saccense platform at depth.

The ~ENE-WSW trending, ~35 km long MB stretches from northeast of Mazara del Vallo to the macroseismic area of the 1968 earthquake sequence. Although geologic and geodetic evidence of deformation are weak, the system is considered responsible for the Mw max 5.7, 1968 Belice seismic sequence. The Mw 4.9, 1981 Mazara del Vallo thrust earthquake occurred few km to the SW of the western terminus of the MB.

The ~NE-SW trending, ~20 km long CCG straddles from off Capo Granitola to east of Castelvetrano, and is composed of two segments. The northern, ~12 km long segment is characterized by an up to 60 m high, and up to 15° steep scarp, which is the fore-limb of a broad fold involving Lower Pleistocene shore calcarenites. On the fold culmination, few synthetic and antithetic thrust splays are present, and one of them is responsible for cm-scale reverse displacement of an early Bronze-Hellenistic road. The segment coincides with a sharp gradient in Differential SAR interferometry (DinSAR and STAMPs) and GPS velocity fields, suggesting active deformation.

Inversion of fault slip-lineation data from structures displacing the archaeological remains yields a ~N110°E shortening axis, consistent with the geodetic shortening direction estimated from GPS differential velocities.

The offshore continuation of the CCG in the Sicily Channel is a ~35 km long, NNE-SSW striking segment that coincides with the Capo Granitola (CGFS) transpressional fault system. An additional transpressional fault sub-parallel to the CGFS, the ~35 km long Sciacca Fault system (SFS), is present offshore Sciacca. Analysis of high-resolution Sparker seismic profiles and of available multichannel seismic profiles show that both the Capo Granitola and Sciacca faults are active. It is likely that either the offshore faults (Capo Granitola or Sciacca) or the onland CCG were the source of destructive events at Selinunte.

A further active structure, the M. Magaggiaro-Pizzo Telegrafo (MMPT) is present to the east of, and strikes oblique to both the SWEST and to the CGFS and SFS transpressional faults.

# Thermal springs in Western Sicily as sensitive sites for the 1968 Belice seismic sequence. A review

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Keywords: Thermal springs, 1968 Belice seismic sequence, Western Sicily.

In Western Sicily there are three low-medium enthalpy geothermal systems, Montevago, Castellammare-Alcamo and Sciacca, with T ranging from 32 to 56°C. Concentrations of main solutes, dissolved gases ( $CO_2$ ,  $N_2$ , He) as well stable isotopes ( $d^{18}O$ , dD and  $d^{13}C_{TDIC}$ ) determined in thermal and cold discharges were used to characterize their feeder aquifers.

The inferred deep end-members of the thermal waters of Montevago and Castellammare-Alcamo suggest that both systems are fed by reservoirs with a  $Ca(Mg)-HCO_3-SO_4$  composition deriving from the mixing between waters interacting with Mesozoic limestones (Ca(Mg)-HCO<sub>3</sub> waters) and waters flowing through Messinian evaporites (Ca-SO<sub>4</sub> waters). A slight contribution (1±3%) of seawater, during groundwater ascent it is also present.

Sciacca thermal springs are fed by a deep reservoir comprising a mixture of 50% limestone waters and 50% seawater. During their rising towards the surface, deep thermal waters mix with shallow cold waters in different proportions.

Although these differences in the chemical composition of the thermal waters, TDIC contents and  $d^{13}C_{TDIC}$  values seems to indicate in all the three geothermal systems in Western Sicily the presence an external inorganic source of CO<sub>2</sub> that would have a  $d^{13}C_{CO2}$  value in the range from -2 to +2‰. This range is overlapping both with the range of the mantle-derived CO<sub>2</sub> typical for Mediterranean areas and with the carbon dioxide produced from thermo-metamorphic decomposition of carbonate rocks. The addition of a deeply-derived carbon dioxide, fully agrees with the model proposed by Caracausi et al., (2004) which suggested in western Sicily a significative contribution of mantle-derived helium degassed from magmatic bodies probably intruded in the crust.

Between 1966 and 1969, significant temporal variations have been recorded in the thermal waters of Acqua Pia (Montevago) and Terme Selinuntine (Sciacca).

Although the data were discontinuously acquired, it was possible to hypothesize a link between geochemical changes and the occurrence of the 1968 Belice Valley earthquake.

Two types of geochemical behavior have been recognized. A permanent change in the chemistry of the Montevago thermal waters was inferred to reflect a modification of the groundwater flow path. Terme Selinuntine spring showed a transient increase in  $pCO_2$  in coincidence with the seismic swarm likely caused by a temporary increase of the contribution of deep CO2-rich fluids caused by the strain release during the 1968 earthquake.

The occurrence of thermal waters in Western Sicily seems to be driven by the main tectonic structures. These seismogenetic structures enable the deep fluids to rise towards the surface (i.e. advective transport), thus making thermal waters in Western Sicily strongly sensitive to changes in the local strain.

## The 1968 Belice Earthquake Sequence, its virtual impact to the temples at Selinunte, SW Sicily

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Keywords: Archaeoseismological modeling, seismic site effects, earthquake-source scenarios.

Selinunte, located at the south coast of western Sicily was one of the first ancient Greek colonies, and underwent enormous building activity around 550 B.C.E. Within a short time span, at least nine classical temples were constructed, measuring in size from 100 to 4,500 m<sup>2</sup> Previous archeoseismological studies presented interpretations for at least two earthquakes that caused partial or complete destruction of some of the temples. However, identification of the earthquake sources has not yet been quantified and only speculations about the nature of the damaging processes were made. Historic reports describe a siege of Selinunte in 409 B.C.E. by the Carthaginians, and the degree of anthropogenic damage to the temples during the attack is also not clear.

In this work we discuss preliminary results of the interdisciplinary SELINUS Project. We chose three locations in Selinunte in close proximity to each other. The temples at these locations (La Gaggera Hill, Acropolis, and East Hill) varied in size and type of structures. We applied active and passive seismic in situ experiments, including the deployment of wireless seismic arrays, to better understand the seismic site effects, which in places proved to be particularly challenging due to the presence of a low velocity sand layer under a strong layer of calcarenite. Since each location has distinct seismic site effects, this study provides an interesting test case for quantitative archaeoseismological modeling. While earthquake sources on several active faults of the "DISS" INGV data base (http://diss.rm.ingv.it/diss/) in south-west Sicily are a threat to the structures in the archaeological park of Selinunte, in this contribution we concentrate on the effects of earthquakes on the fault system that caused the 1968 Belice earthquakes. We combine the site effects with earthquake-source scenarios and with parametric discrete element models of temple buildings. The method in this study makes good use of the differently-structured temples as large seismoscopes and addresses the question, what effect an earthquake like the 1968 would have had on the temples. Also the assumption of larger earthquakes on the same fault system can be studied. Thus, we can test the plausibility of existing hypotheses about the damage process and better quantify the source parameters of potentially damaging earthquakes and reveal data important for the present earthquake safety of the archaeological park.

# The gypsum karst system of Santa Ninfa (Belice valley) in the framework of the neotectonic activity of south-western Sicily

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Keywords: caves, Inside Fault Observatory, neo-tectonics.

The karst system of Santa Ninfa develops in an outcrop of Messinian gypsum extending for about 15 km<sup>2</sup>, located in the hearth of the zone struck by the 1968 seismic sequence of the Belice valley. This system is composed of a huge variety of surface and sub-surface karst landforms, with dimensions from centimetres to kilometres. Surface run-off is mostly catch by sinkholes, and supplies a well-developed network of hydraulically active caves. Groundwater circulation, as well as dimension and orientation of karst galleries, is mainly controlled by structural lineaments and, at a lesser extent, by the orientation of litho-stratigraphic discontinuities. Karst galleries are preferentially oriented SW-NE, and secondarily SE-NW, in good accordance with the directions of the main neo-tectonic lineaments identified in south-western Sicily. The fundamental role played by tectonics in controlling the development of the cave network is highlighted by the comparison between total length and extension of the feeding areas of hydraulically active caves. The overall development of these caves shows no evident relationships with the total surface of the feeding catchment areas; sink-holes draining surface run-off developing along bedding planes are always of modest dimensions, even if the total drained area is significantly high. On the contrary, caves showing clear signs of a tectonic control usually develop in length much more than the previous ones, even if supplied by modest catchment areas. The above mentioned considerations remark the potential interest of the Santa Ninfa karst area in the framework of a monitoring system of neo-tectonic activity in south-western Sicily; in fact, the presence of caves developing along fault planes, and accessible by humans, allows the implementation of an observational system that extends to the "Inside Fault Observatory" the "Near Fault Observatory" concept already applied in other seismically active area of Italy, as the High Tevere valley.

# Gibellina, Montevago, Salaparuta and Poggioreale: about built heritage underutilization and possible urban future

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Keywords: post-earthquake reconstruction, urban revitalization, built-up volumes analysis.

Disasters like earthquakes affect dramatically the construction of place identity. Urban settlements generate complex social structures, they are not just scenarios where the functioning of city takes place. 'Interrupted landscapes' cannot be merely reconstructed. Post-earthquake reconstruction lies in between community social identity protection and urban planning approaches to renewal or rebuilding. This paper focuses on the four urban centres of Gibellina, Montevago, Salaparuta and Poggioreale that were reconstructed in a different place after the Belice earthquake emptied the historical centres. By using ArcGis functions the built environment of the four settlements has been analysed in terms of built up volumes, land uses and inhabitants. The most relevant outcome is an impressive underutilization of the built up heritage. Data analysis triggers critical considerations on urban strategies and choices that drove the reconstruction, and to discussions on long term effects caused by the 1968 event. Understanding what happened, looking backward to the fifty years long history, is the basis for imagining the future of this area. Based on available National Census data (2011), the capacity to host residents in the built up areas appears to be much more higher than the real needs, considering that population in this centres has been continuously decreasing. For example, Gibellina lost more than 200 inhabitants between 2011 and 2017. The post earthquake reconstruction was mainly based on the simple idea of reproducing the pre-seismic social and economic dynamics, when the Belice was a very active rural area. This paper presents the case study of the four rebuilt settlements trying to imagine possible directions of a revitalisation of this area, taking into account the present and future challenges for local authorities, which are responsible for managing a massive quantity of built area, facing increasing maintenance costs and the risk of progressive abandonment of neighbourhoods. Taking into account other recent experiences of urban revitalization in inner areas of Southern Italian regions, the aim of the paper is to discuss about the possible future of the Belice new centres from a town planning perspective.

# **Session S40**

# The role of abiotic and biotic soil components, environmental materials and factors, and physical evidence in criminal investigations, environmental crimes, and legal system

Conveners AND CHAIRPERSONS Roberta Somma (Università di Messina) Eva Sacchi (Animal, Plant and Soil Traces Working Group of European Network Forensic Sciences Institutes - ENFSI) Fabio Tortorici (Fondazione Centro Studi, Consiglio Nazionale dei Geologi) Luca Trombino (Università di Milano)

#### Characterization of bone taphonomy on archaeological and modern human remains by FT-IR and BSE-SEM

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Keywords: bone taphonomy, FT-IR, BSE-SEM.

Both in the bio-archaeological and in the forensic context, it is extremely important to understand the taphonomic processes affecting the human remains, in order to provide the estimation of the post mortem interval (PMI) or to reconstruct the causes of death or the environment in which the bodies were buried.

Peri and post mortem events always leave marks to be interpreted in the light of the state of conservation or degradation of the skeletal remains. Because the bone tissue is an intimate association of mineral (carbonate-hydroxyapatite) and organic components (collagen) arranged in an ordinary structure, different levels of degradation are possible, mainly depending on the environment in which the bones are deposited. Moreover, the taphonomic alteration can occur at different scale of observation, i.e. macroscopic, microscopic and ultramicroscopic, and at different point of view, i.e. biomolecular and chemical..

The present work evaluated the characterization of the alteration of the mineral and organic phases, and their histological assessment, of several human bones coming from different burial environments of the Milan area, with ages spanning from the Late Roman period to our time. Since the conventional anthropological methods are often not enough the evaluate of taphonomic bone pathways related to the time since death and burial settings, in this project we focused on the advantages of applying two typical Earth Sciences analytical techniques, as FT-IR and BSE-SEM, to carry out these information.

Fourier transform infrared spectrometry (FT-IR) was performed to quantify the preservation of mineral and organic content, by the measurement of the absorption intensities of collagen (v1Amide I), phosphate ( $v^3PO_4$  and  $v^4PO_4$ ) and carbonate ( $v^2CO_3$ ), and to provide the assessment of crystallization (IRSF) of hydroxyapatite over time. As results of FT-IR analysis, a general decrease of organic and carbonate content with age was observed, whereas the bone crystallinity increased from the most ancient bones to the recent ones. Moreover, bone crystals from archaeological contexts appeared generally larger, with a more ordered structure, than fresh bones.

Scanning electron microscope -SEM- was employed to visualize at high resolution the taphonomic alteration of the bone histology. Bone histology showed a heterogeneous conservation among archaeological bones in BSE-SEM, whereas modern samples were all well preserved.

Therefore, this study proves that chemical and ultramicroscopic changes follow independent paths, and the estimation of the taphonomic process need multiple level of investigation since affects the bone tissue differently at different scale.

# Unpredictability of the detachment of a clay block from the excavation front of a tunnel

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Keywords: Forensic geology, Environmental crimes, Waste dumps.

During the construction of a tunnel, the detachment of a clay block from the excavation steep front caused the death of a workman. The aim of the legal advice was to verify the predictability of the detachment responsible for the accident, which would have made the construction company responsible for the death of his employee.

Detailed geological and geomorphological analyses accomplished on the studied kinematic detachment made it possible to establish that it was due to a fall landslide phenomenon (Varnes, 1978; Cruden & Varnes, 1996). The predisposing cause of this fallwas attributed to the combination of a number of factors linked to the rather complex geological-stratigraphic conditions associated with the occurrence of joints in the clayey mass and to the effects of the local water circulation in the subsoil; while the determining cause was attributed to the ordinary vibrations caused by the safeguard of the excavation front.

Kinematic modalities typical of the initiation of fall landslides, being characterized by very to extremely rapid movements hindering to distinguish the precursor phases of the movement (micro-movements or deformations preluding to possible important events), allowed to establish that the detachment of the clay block, being a fall landslide, had to be included in the category of unpredictable events.

Cruden, D.M. & Varnes, D.J. (1996): Landslide types and processes. In: Turner A.K. & Schuster R.L. Eds. Landslides investigation and mitigation. Transportation research board, US National Research Council. Special Report 247, Washington, DC, Chapter 3, 36-75.

Varnes, D.J. (1978): Slope movement types and processes. In: Schuster R. & Krizek R. Eds., Landslides, analysis and control, Transp. Res. Board, Nat. Acad. Of Sc., Washington D.C., Special Report 176.

#### Crimes against the environment: how to deal with them

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Keywords: Forensic geology, Environmental crimes, Waste dumps.

In the case of environmental crimes, to correctly answer to magistrates court questions it is essential to know the binding legislation and to plan an efficient investigation project after preliminary judicial inspections. An efficient investigation project must consider: i) Collection of documentation and the related analysis; ii) Multi-time reconstruction of the modifications experienced by the territory; iii) Classic geological survey and photographic documentation; iv) Sampling and consequent geochemical analyses and geophysical prospecting techniques. The collection of documentation includes papers on projects, authorizations, landscape restrictions, local strategic plan, etc., and also certified imagery, topographic maps, DTMs and DSMs covering a wide time interval and usable in GIS. The classic documental analysis must be accomplished at the beginning of the investigation, as it allows the advisor to understand the site history and to better address the consequent analyses. The multi-time reconstruction is very important and it may be realized by means remote-sensing analysing satellite and aerial imagery. It is a low cost analysis, in economic and time terms, necessary as it allows: 1) to analyse the history of the site and of the surrounding areas, as the environmental matrices may be influenced by anthropic actions made in neighbor zones; 2) to ascertain the veracity of testimonies, projects, documentations; 3) to discover past crimes that may have influenced the actual site state. Classic geological survey is fundamental to characterize several geological aspects as those related to lithology, geomorphology, hydrogeology, geotechnics, structural geology, etc. This survey, accompanied by a detailed photographic documentation, is used to describe the actual state of the site and when possible to compare this state with previous site state. It is important to correctly plan the most appropriate sampling scheme and sample number to take in the site and outside of it, to be able to furnish a data really representative of the site, possibly to be compared with samples outside the site not affected by pollution. Analyses of the different environmental matrices and the reconstruction of the subsoil features by means geophysical prospecting techniques are also crucial and must be correctly established. It is of paramount importance in this stage of the judiciary procedure that advisors are able to correctly understand which of the planned inspections must to be or not pledged in consultation with the defense according to law. As regards structures (dumps, incinerators, purifiers, etc.) it is important to acquire information on the Best Available Techniques of the BAT Reference, as eventual anomalies may prelude to environmental crimes...

Finally, it is fundamental that in the magistrate/advisor fiduciary relationship, the advisor plans only essential investigations that the magistrate has to authorize as essential to construct the crime evidence.

#### A case study of environmental disaster

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Keywords: risk analysis, waste dump, eastern Sardinia.

This paper deals with the preliminary results of a study accomplished in the Ogliastra (eastern Sardinia), in order to plan interventions necessary for the permanent securing of a waste dump and the first emergency measures taken for reclaim and safeguarding of a pond located downstream of the dump where mollusk farming activities were present. In the past the waste dump site was a quarry for extraction of inert materials. The site was later assigned to waste disposal over a time lapse between the 1984 and 1996 (date of the dump closure). The risk analysis showed that the dump surface was characterized by a surface of about 55,000 m<sup>2</sup> with a depth of about 5 m under the ground level. The roofing system consisted of a layer of natural soil of limited thickness, whereas the waterproofing system on the dump bottom and walls was not found, except the presence, exclusively on the bottom, of an inhomogeneous layer of silty-clayish soil, probably deriving from the dredging of the pond. The water table was in the dump at a depth of about 2.5-3.6 m from the ground level outside of it. The outflow direction was from SE to NW, i.e. towards the pond downstream of the dump. Consequently part of the waste was stored in the saturated area and locally under the pond level. The waste volume was evaluated in about 100,000 m<sup>3</sup> of which about 50,000 m<sup>3</sup> under the groundwater level. The dump is currently abandoned and included in the list of sites to be subjected to reclamation activities with priority actions.

Analyses of different environmental matrices sampled in the dump and the surrounding areas evidenced in the dump leachate and groundwater the occurrence of dump related contaminants exceeding the regulatory limits (Legislative Decree 152/06), evidencing pollution especially in the downstream pond affected by mollusk farm. According to the recent Law n. 68 of 22th May 2015 on the "Crimes against the environment" five new crimes were introduced in the penal code: environmental pollution, environmental disaster, traffic and abandonment of radioactive material, control impediment, and omitted reclamation. On the base of this law, the evidenced pollution of the site and of the downstream pond affected by mollusk farm, being configurable as a case of offense to the public safety, may be consequently configured as a case of environmental disaster.

# Environmental crimes and advisors: the importance of binding legislation and technical knowledge

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Keywords: environmental crimes, Best Available Techniques (BAT), BAT Reference documents (BREF)

In order to identify environmental crimes, it is required to have both an in-depth knowledge of the binding legislation and an appropriate technical knowledge concerning the activities and environmental management procedures adequate.

The instruments used to satisfy the verification / audit of the environmental management comply with the International Standards of the ISO 14001 and ISO 19011 Series, while for the plant engineering (landfill, purifier, incinerator, petrochemical refinery, steel mill, cement factory, plastics industry, etc.) it is necessary to know the Best Available Techniques (BAT) contained in the BAT Reference documents (BREF) for each type of industrial activity.

A successive investigation phase consists of the documental analysis related to: i) the environmental legislative obligations (such as the authorizations to discharge waste water, atmospheric emissions and compliance with the quantitative limits established by law); ii) the chemical-physical-biological data contained in the test reports; iii) the authorizations for waste management; iv) the Integrated Environmental Authorizations and annexed prescriptions; v) the waste forms and registers; etc.

As regards to offenses to the environment due to illegal activities related to abandonment and burial of hazardous waste, radioactive substances, waste from heavy industry, it is necessary to inspect the territory and to use investigation technologies allowing to analyse the different soil layers and sediments to detect possible thermal (Infra-Red imaging cameras) and biological-chemical-physical anomalies (field survey and laboratory analyses), and/or the eventual occurrence of  $\alpha$ ,  $\beta$ ,  $\gamma$  radiations (Geiger counters). The use of Geographical Information Systems (GIS) in environmental crime investigation may assist advisors/law enforcements to ascertain anomalies depending on possible spilled or illegally disposed polluting materials. Indeed, dedicated software such as ArcGIS allows to superimpose and cross-reference various geographic factors/entities characterizing the environmental crimes, such as geological (soil grain-size, texture, colour, thickness, etc.), geomorphological, and hydrogeological features, the vegetation state, the urbanizations, chemical data, etc.

## The utility of ground-penetrating radar in the discovery of clandestine burials

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Keywords: ground-penetrating radar, clandestine burials, geoforensics.

Burial is a relatively common method of hiding a corpse, thus, in the field of forensic investigation, the identification of clandestine graves is a very important task. Multiple forensic disciplines, as, for instance, microtopography, botany or archaeology, can provide valuable assistance in finding clandestine graves. Moreover, the ground-penetrating radar (GPR) method has recently been introduced as a technique in the detection of clandestine burials, and, in order to evaluate its potential in an operative search scenario, the following experiment has been carried out.

A total of 11 pig carcasses were buried in two areas, the first one with a grass vegetal cover, the second one with a clear wood vegetal cover, but both presenting a similar soil composition (i.e. Dystric Leptosols, according to FAO-based classification systems). The carcasses were subsequently exhumed at regular intervals, ranging from 2 to 111 weeks, and a systematic GPR analysis of the burial sites has been carried out before each exhumation.

The ground-penetrating radar technique proved to be useful in recognizing anomalies at the chosen depths of burial; moreover, these anomalies appeared to be dependent on the state of decomposition of the carcasses, producing only slight anomalous readings in the presence of already skeletonized remains: at 92 weeks from burial the detected GPR signal was weak and at 111 weeks GPR survey offered no helpful information in order to identify the burial location.

In this particular context, the experiment, determined that the ground-penetrating radar technique has been successful only in the presence of recent burials, highlighting the need for a multidisciplinary approach in the operative search for buried human remains.

#### An European network for improving Forensic Science

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Keywords: Forensic Geosciences, Geoforensics, Homogenization, Result validation.

Forensic Science is a relatively recent branch of science. As with all new research fields, it had many different approaches at the beginning, while different laws applied in different countries increased such differences (e.g. Fingerprints consistency). For a long time, this discipline suffered the lack of a generally accepted literature and of result validation. Also, in the past, results were frequently accepted in court only on the basis of authoritative opinion of the expert and not on the basis of well-established procedure. All these problems were even more obvious in Forensic Geosciences, where very often results are expressed in terms of probability and not "beyond any reasonable doubts".

Over time, the Forensic Science community, while increasing in number and developing its experience, became aware that a more scientific and consistent approach was necessary in dealing with evidence; as a result of this a European network of researchers and laboratories was founded in 1995: the European Network of Forensic Science Institutes (ENFSI). At present the network includes 68 member laboratories, distributed across 36 countries geographically located within Europe, covering a broad range of forensic fields. ENFSI also includes 2 Standing Committees (Quality and Competence Committee and Research and Development Standing Committee) and is subdivided into 17 expert working groups covering most of the field of Forensic Science (e.g. DNA, documents, drugs, explosives, etc.). One of these groups, the "Animal, Plant and Soil Traces Working Group", includes a large part of the basic branches of Forensic Geosciences. The work of this expert working group is to sets guidelines, best practice manuals and standard operating procedures. In order to achieve these goals (to homogenize procedures, disseminate methods, validate labs and improve results), all of its members participate in periodic collaborative exercises and proficiency tests.

This means that the Forensic Geosciences is at last exiting a pioneering phase that lasted too long, and it's starting to reach the status of a true science.

# Forensic geoscience today: which future prospects

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Keywords: Geoforensics, Academic Education.

Geoforensics is a branch of Forensic Sciences dealing with the applications of the principles of Earth Sciences in order to solve criminal cases; the aim of Geoforensics is therefore to assist in criminal justice by providing useful information to investigators. The physical contact between a victim and a suspect may produce a transfer of trace materials; this transfer is the base of Forensic Sciences and is known as Locard's exchange principle. Forensic geologists identify and compare trace materials, such as soils, to establish if there is a common source or to discover their provenance. Comparative, exclusionary, and predictive analyses of forensic soils represent most of the work a forensic geologist is required to do: typical examinations include comparison to assess a common origin, identification of an unknown material, and assessment of the geological origin or geographic attribution of a material. Comparing trace evidence that could be transferred during the commitment of a violent crime may assist in: i) establishing if soil sampled on the suspect clothes or shoes is or isn't associated with physical evidence related to a victim or to a crime scene, *ii*) verifying the veracity of a declared alibi, *iii*) identifying the site where a victim or suspect walked or was buried, or a car passed by. These competencies are well developed, especially in the USA where the FBI Laboratory represents one of the largest crime labs. There are only a few public crime laboratories of Law Enforcements, providing forensic geological services. The FBI mineralogy group realizes laboratory analysis and field assistance. Trace evidence examined are soil, glass, building materials, and gemstones. In Italy forensic geologists are still too few (only about 15). Only a minority of them are working in the Law Enforcements' crime labs (two or three), whereas most of them are freelances. Some of them recently were trained thanks to a master course in "Forensic Geology" held at the Messina University. Thanks to this unique initiative, Geoforensics achieved for the first time the status of forensic science in the Italian academic field. Moreover several annual events of a summer schools in Geoforensics were organized by the Messina University, establishing itself as the only active Italian public university devoted to this topic, open to undergraduates, graduates, and law enforcements from the 2015 to date. Despite these academic initiatives, there is still a lot of work to do with magistrates, law enforcements, lawyers, and scientists, to highlight the importance to apply these competencies in assisting law enforcements in criminal cases, as well as to employ more forensic geologists in law enforcements crime labs.

# Relevance of telethermography in waste dumps

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Keywords: thermography, waste dump, geomembrane.

The thermography may be very useful in the solution of environmental crimes, as the study of the thermal anomalies may assist technical advisers to understand some features of the waste dumps. The analysis of the thermal anomalies is traditionally devoted to identify the leaks of biogas, as depending on exothermic chemical reactions. A well-advanced application of thermography in the study of waste dumps was experimented. Thermographic analysis was realized in several waste dumps during the daylight and the night. Waste dumps with protection provided of capping with geomembranes resulted to show consistent thermal anomalies during the daylight disappearing during the night. Conversely, waste dumps without this capping did not exhibit peculiar thermal anomalies during the daylight and the night. The consistent thermal anomalies detected depend on the overheating of the geomembrane during the daylight notwithstanding the geomembrane cover of the superficial sediment layer. This result is very interesting as the study of thermal anomalies may assist technical advisers to understand with a low cost, rapid times and not-destructive analysis if the waste dump is capped by a geomembrane.

#### Exposure to Radon and National Radon Plan in Italy by Directive 2013/59/Euratom

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#### Keywords: Radon, Illegal exposure.

It is well known that exposures to Rn-222 and its progeny (commonly known simply as Radon) is source of health hazard, either for the workers or the public. In literature there are evidence of epidemiological studies pointing out the statistically significant increase of lung cancer risk from prolonged exposures to indoor radon.

The Directive 2013/59/Euratom concerns basic safety standards for protection against the exposure to ionizing radiation. Before this, Directive 90/143/Euratom was to be incorporated into the binding requirements of the Basic Safety Standards while leaving enough flexibility for implementation. This new Directive applies in particular to the exposure of workers or members of the public to indoor radon, the external exposure from building materials and cases of lasting exposure resulting from the after-effects of an emergency or a past human activity.

It is stated that Member States shall establish national reference levels for indoor radon concentrations in workplaces for the annual average activity concentration in air and shall establish a National Action Plan, updated on a regular basis, addressing long-term risks from radon exposures in dwellings, buildings with public access and workplaces for any source of radon ingress, whether from building materials or geological factors as water or soil. Indeed, it is noteworthy that volcanic regions and active fault zones may be at high natural radon radiation risk. Exposure to natural radiation sources includes: indoor exposure to radon and thoron, in workplaces, dwellings and other buildings; indoor external exposure from building materials.

There are strategies for conducting surveys of indoor radon concentrations or soil gas concentrations for the purpose of estimating the distribution of indoor radon concentrations, for management of measurement data and for the establishment of other relevant parameters (such as soil and rock types, permeability and radium-226 content of rock or soil).

It is important the delineation of areas with potentially high exposure to radon, since it is a basis for the establishment of reference levels for dwellings and workplaces, assignment of responsibilities (governmental and non-governmental), coordination mechanisms and available resources for implementation of the action plan, strategy for reducing radon exposure in dwellings, for facilitating post construction remedial action, for preventing radon ingress in new buildings, including identification of building materials with significant radon exhalation to long-term goals in terms of reducing lung cancer risk attributable to radon exposures.

In this paper the AAs discuss also about the fact that in Italy there is legislation only in workplaces (Law N. 230/1995 updated by law N. 241/2000). It is to notice that directive 89, 90, 96 are repealed and it is necessary that Member States transpose this directive since February 6, 2018.

## The Aldo Moro murder case forty years after: New investigative implication on Moro's last days

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Keywords: Aldo Moro, Forensic geology, sands.

Gianni Lombardi's examination of the evidence linked with the murder of Italian Prime Minister Aldo Moro is considered as a masterpiece of forensic geology.

Forty years ago on May 9, 1978 the body of Aldo Moro was found in Via Caetani at Rome inside the trunk of a Renault 4. The volcanic beach sands, polyester fragments, bitumen, and plant remains (unknown samples) sampled on Moro's clothes, shoes and on the Renault 4 were analysed by G. Lombardi and V. Giacomini for the investigating authority. These sands were compared with 92 other sand samples (known samples) taken along a 150 km long transect of the Tyrrhenian coast in Latium, from Tarquinia to Terracina (including Ostia). Forensic comparative analysis suggested that the unknown samples were similar with supratidal marine sands from the seashore between Focene and Palidoro. The *capitulum* of *Centaurea aspera* found on Moro's trousers and the bitumen from Moro's shoe sole as well as physical evidence from the Renault 4 indicated that (i) Moro walked on this seashore and (ii) the Renault 4 passed on by, shortly before Moro's homicide. However, the investigative implications of this expertise were not fully understood as police did not discover the terrorists' hangout in the identified area (Lombardi, 1999).

The terrorists declared during their interrogations and more recently in a television interview that the sands and bitumen were taken from the Ostia beach and put on Moro's clothes to mislead the investigators. This declaration contrasts with the results from Lombardi's study and with the difficulty to explain how this material could also be in the car's fenders, tires, and car frame without placing the car on the site.

Recently, the contents of the terrorists' message n. 13 were divulgated on mass media (Saita, 2015). It highlighted a new investigative implication revamping the meaning of the Lombardi and Giacomini data related to the last days of Moro. The message suggests that the terrorists' original plan on the site where to leave Moro's body was elsewhere. Moro's body was not meant to be found in Rome, but around the Forte San Martino in Genoa, one of terrorists' outposts.

Under this new perspective, physical evidence reported in Lombardi (1999) may suggest that Moro walked on the Focene-Palidoro beach, not because he was imprisoned there but as a consequence of a brief stop during a failed attempt of terrorists to transfer by car Moro from Rome to Genoa shortly before his homicide.

Lombardi, G. (1999): The contribution of forensic geology and other trace evidence analysis to the investigation of the killing of Italian Prime Minister Aldo Moro. Journal Forensic Sciences, 44, 634-642.

Saita, F. (2015): Caso Moro, spunta audio inedito. <u>http://www.adnkronos.com/fatti/cronaca/2015/09/30/caso-moro-</u> spunta-audio-inedito-esclusiva-adnkronos\_9VdeNE1pXIQJgtavJeEAKK.html.

# A contribution to the search of illegal concealments: A GIS-based quantitative approach to define a prioritization system

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Keywords: GIS, illegal concealments, search prioritization systems.

An innovative GIS-based approach to follow during ground searches for illegal concealments (clandestine graves, wastes, weapons, etc.) is based on the Red-Amber-Green (RAG) prioritization system implemented by means of GIS technology. A strategy for the ground search of clandestine sites must take into accounts that most offenders search burial sites with the following characteristics: (i) soft and thick soils, (ii) a plain surface or gentle slope, (iii) little surface changes in soil aspect, (iv) hidden locality from potential eyewitnesses, (v) familiar location, (vi) easy access on foot or by vehicle, (vii) reference points to be able to monitor the burial site, (vii) stable areas. Therefore, the main suitability factors/entities influencing the offender's burial-site choice are: 1) diggability, 2) landscape/slope, 3) vegetation, 4) human-made structures, 5) geomorphology, and 6) visibility. The procedure develops a GIS-based Color-coded Prioritization System that is able to edit both the RAG maps of above-cited factors/entities and the search scenarios (Somma et al., 2017). These latter are based on cross-referencing RAG maps of these factors in order to obtain cumulative suitabilities identifying high-(Red), medium-(Amber), and low-(Green) priority areas. In the search scenarios, it is assumed that: (i) the Red class is applied for areas in which all entities are red; (ii) the Green class is applied for areas in which at least one entity is at low suitability among the three RAG classes; (iii) the Amber class is applied for areas in which at least one entity is amber among the Amber and Red classes. The "search scenario without the visibility" will be the most effective one if the concealment occurs at night; it will be the most conservative as experimental scenarios indicate that the Red and Amber areas may extend from 51.8 to 69.4 %. Differently, the "search scenario with the visibility" will be most appropriate if the concealment occurs in daylight; experimental scenarios indicate that the Red and Amber areas may extend from 11.5 to 35.2 % of the total search zone, considerably assisting searches. For efficient ground searches it is fundamental to produce more search scenarios: depending on offender's modus operandi and behavior, one of them is more suitable than the others.

Somma, R., Cascio, M., Silvestro, M. & Torre, E. (2017): The application of a GIS-based prioritization system for the search of a simulated clandestine grave. The Journal of Forensic Sciences. DOI:10.1111/1556-4029.13677.

# Time-dependent evidences of decomposition and permanence in soil in experimental burials: a geopedological approach

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Keywords: forensic science, forensic geopedology, clandestine graves.

A buried body not only determines an environmental response at the deposition site but it is also affected by the soil. Thus the importance of the role played by soil scientists in the modern forensic sciences is increasing, in particular when buried human remains are found in different environmental situations. This study is part of a wider project, in which an interdisciplinary team worked on swine carcasses buried in an open site (Northern Italy), focusing on decomposition and environmental responses to the burial (Davenport et al., 1992). The present work focuses on the micromorphological (petrographic microscope) and ultramicroscopic (SEM-EDS) cross characterization of the osseous tissue, in order to describe the alteration pathways in bones due both to decomposition and permanence in soil.

These methods allowed the identification of different alteration figures in bones. Magnesium phosphate  $(Mg_3(PO_4)_2)$  crystallizations were observed in the osseous tissue fissures or inside the Haversian canals of specimens whose soft tissues are still present on bones. Thus, they are probably linked to decomposition of bones and soft tissues (Zofkova et al., 1995). It were also recorded significant sulphur levels in a lumbar vertebra. This data seem to be related to hydrogen sulphide (H<sub>2</sub>S) fixation in the bone tissue closest to the abdominal area, from where decomposition gases begin to diffuse (Goff, 2009). Instead, metal oxide concentrations were found in the form of unusual violet-blue colorations, which are probably evidence of the soil penetration in bones (Landuyt, 1990) also testified by the presence of mineral grains enclosed in the osseous tissue. Additionally, the results of graves soil analyses show periodical increases of phosphorus (P) level due to its release from the inhumed corpse, thus testifying the occurrence of P transfer from buried remains to the soil.

The results underline the possibility of identifying both time-dependent markers of decomposition and indicators of permanence in soil in buried bones. In addition, the techniques here used open a door on the knowledge of mineralogical changes of the bone tissue interacting with the soil, also allowing to study a possible initial formation of vivianite minerals.

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# Phosphatic impregnations on soil particles in experimental burials: ultramicroscopic characterization and environmental control on their persistence

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Keywords: forensic science, forensic geopedology, clandestine graves.

Burial is a relatively frequent manner of disposing the body in murder cases. Geo-forensic investigations not only provide useful guides for clandestine graves localization, but also allows to analyse many aspects of the inhumation site (Schultz et al., 2008). This study is part of a project in which an interdisciplinary Italian-team has been working on experimental burials of pigs in a uniform area, in order to obtain new data on the environmental responses to the inhumation site over different time intervals (Zangarini et al., 2016). The present work is strictly focused on the ultramicroscopic (SEM-EDS) characterization of the phosphatic impregnation (by body fluids) in soils sampled under the eleven swine carcasses dug up at different intervals.

Both the natural soils and the filling of the ditches overlying the carcasses resulted phosphate free. This is caused, as expected, by the acid soil parent material. On the other hand, in all the soil specimens sampled below the carcasses, numerous phosphatic features have been identified by SEM observation in the form of: coatings and infillings on sand grains, coatings on vegetal remains, impregnations on crumby microaggregates, organominerals associations. Such phosphatic features originate from the impregnation by body fluids, resulting from the decomposition of the swine carcasses (phosphorus source) on the soil mineral and organic particles. These phosphatic impregnations can thus be used as indicators of the former presence of decomposing body in the overlying soil material even in absence of the body itself (Tibbet & Carter, 2008).

Furthermore, the described phosphatic features show variable trends of persistence in the soils sampled below the swine carcasses. This variability could be induced both by the different grain sizes of the impregnated soil and by the time factor, i.e. the post burial interval, but these factors must be tested more accurately in future works. The most effective environmental signal recorded by the persistence of the described phosphatic features seems to be related to the moisture conditions of the season of exhumation, which are consistent with the moisture control over the decomposition in soils.

Geopedology is a science rich in variability with a great potential in the reconstruction of many forensic cases. However, further experiments may aid to clarify the pathways of the described phosphorus precipitation and leaching.

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# Session S41

# Planetary evolution: insights from geological studies, meteorite analyses and terrestrial analogues

Conveners And CHAIRPERSONS Lucia Marinangeli (Università "G. D'Annunzio" Chieti-Pescara) Valentina Galluzzi (INAF, Roma) Cristian Carli (INAF, Roma)

# Biotic to abiotic mineral precipitation in continental hydrothermal settings: a potential journey from early Earth to extraterrestrial planet

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Keywords: Travertine, microbial mat, organomineral.

Earth's biological evolution and environmental history are intimately connected. It is commonly accepted that microbes and virus dominated the early Earth biological landscape and played important roles in global and small-scale biogeochemical cycling and evolution of life. Models of Earth's environmental history and biological evolution endorse tectono-magmatic driven hydrothermal-spring in continental settings as one of the Earth's most primitive ecosystems. Defining how life adapted to specific environmental hot-spring conditions and which is its involvement in mineralization processes from the modern perspective will open up the possibility to improve our understanding of the impact of life on the Earth's systems and its permanent imprint in the geological records. Due to similarity with other planets, hot-spring deposits could be also of major importance to astrobiology.

In view of all the above findings, a multidisciplinary investigation on four modern hydrothermal spring travertine deposits located in Central Italy, formed by Ca (Mg)-SO<sub>4</sub><sup>2-</sup>-HCO<sub>3</sub><sup>-</sup> waters at temperature ranging from 34 to 50°C and pH values from 6 of ca. 7.5, have been conducted. The integrated approach of this research, essentially based on sedimentary, petrographic, geochemical, mineralogical, petrophysic and geomicrobiological principles, has been considered critical to gain exhaustive answers concerning the complexity of hydrothermal spring-related carbonates.

The spectacular occurrence of authigenic mineral precipitation of calcite and aragonite and minor amount of gypsum, sulfur and pyrite in association with microbial mats and biofilms provided an important opportunity to evaluate bio-geochemical and physicochemical factors that have direct impact in carbonate precipitation. Molecular analyses indicate a high biodiversity of the microbial mat communities characterized by diverse morphologies and pigmentations with a wide range of metabolic processes, varying from anaerobic to aerobic.

Results suggest that the complex microbial community interfaces with the environmental abiotic factors to form peculiar sedimentary structures characterized by a wide range of architectural and facies patterns, including mound-shaped build-up. A large variety of fabric types reflect precipitation processes due to interplay between abiotic and biotic (i.e., biologically induced by microbial metabolic process or simply influenced by nucleation on microbial biofilm substrate) and/or a combination of both processes, which are subsequently modified by diagenesis. High magnification SEM analysis, showing the mutual presence of EPS, microbes, virus-like particle and organominerals, revealed that biological activity and degradation of organic matter play a fundamental role in the travertine formation.

This study will help the definition of potential bio-signatures as proxies for life in Earth and extraterrestrial environments.

### Proclus Crater: Spectral variability within Lunar Highlands

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Keywords: Proclus Crater, Plagioclase, VNIR Hyperspectral.

Recently, the hyperspectral-imaging instrument M3 onboard Chandrayaan mission global covered the lunar surface (Pieters et al., 2009), and detected the presence of an absorption band at ca. 1250nm, due to  $Fe^{2+}$  transition in PL, in central peaks of impact craters (e.g. Cheek et al., 2012). Moreover, regions embedded in the Highland, characterized by mafic minerals, has been observed (Yamamoto et al, 2015). Here, we analyzed M3 reflectance spectra of Proclus crater, a 28 km crater situated in the west of Mare Crisium, were high amount of PL have been previously detected (e.g.Donaldson-Hanna et al., 2014). We first classified the crater in different spectral regions, using the Spectral Angle Mapper (SAM) method, with a spectral library build by means of Purity Pixel Index (PPI), basing on the different spectral properties in the reflectance data. Then, we related the spectral parameters of each region to the mineralogical composition. To this purpose, the M3 data have been compared with laboratory spectra acquired on well characterized mixtures of PL and mafic minerals, such as pyroxene (PX) and olivine (OL) (e.g. Serventi et al., 2016 and references therein). We recognized regions with different spectral behaviors: 1) PL regions located mainly in the crater walls; 2) PX regions in both the walls and the floor of the crater; 3) OL region in the south-east portion of the crater walls; and 4) PL (>90%)+PX regions in the crater wall. Here we have highlighted how a comparison with laboratory spectra can strongly help to obtain information about the mineral content and composition of a planetary surface.

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### Unravelling the tectonic contribution to the internal architecture of the Mars Polar Layered deposit

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Keywords: Mars Polar Layered deposits, Hybric Cellular Automata, tectonic modeling.

The internal architecture of the polar layered deposits (PLD) of the Martian ice caps closely resembles the internal layering of the East Antarctic Ice Sheet (EAIS). Cross section profiles based on data from the Shallow Subsurface Radar (SHARAD) instrument on NASA's Mars Reconnaissance Orbiter shows the internal stratigraphy of the PLD (Phillips et al., 2011; Smith et al., 2013; Foss et al., 2017; Putzing et al., 2018) similar to the layered geometries evidenced by radargram from radio echo-sounding in Antarctica. The PLD have been recognized as stratigraphic evidence for migration caused by wind transport and erosion (Smith et al., 2015). Mechanisms responsible for layered deposits of Mars are still under debate (Guallini et al., 2017)

The role played by the interaction between the active bedrock tectonics and the ice sheet dynamics in East Antarctica was highlighted by the Hybrid Cellular Automata (HCA) modelling technique (Cianfarra, 2006). With a similar approach the HCA numerical method (Cianfarra and Salvini, 2017; Cianfarra and Maggi, 2017) allowed to kinematically simulate the internal architecture of the layered deposits from both the north and the south Martian ice caps. Results from the numerical modeling showed that tectonic movements within the ice associated to the activity of normal faults play a key role in present day architecture of the Martian ice cap stratigraphy.

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# Lumino: a datation instrument for the surfaces of Mars and the Earth

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Keywords: Planetary surface, datation, luminescence.

Luminescence dating techniques are well established for providing sedimentation ages of deposits on Earth. Recent developments showed the feasibility of luminescence dating for sediment analogues to Martian deposits. An instrument providing such data on Mars will be a useful tool in decision making, pre-screening of samples for sample-return missions as well as for in-situ investigations of e.g. regolith formation and/or dune motion. The LUMINO project addresses the technological and economic viability of a leading-edge instrument for dating Mars samples: a miniaturized instrument for in-situ analysis and assessment based on luminescence methods. Due to the development of this innovative technology, in addition to planetary exploration applications, LUMINO also addresses terrestrial field applications as a light and portable dating instrument in geology and archaeology.

For the LUMINO project a trade-off analysis for the components of luminescence dating instrumentation will be carried out. The project activity will also include a State of Art review of critical technological parts, such as:

- Excitation unit: to stimulate the sample with the optimal material dependent wavelength, and by pulsing of the stimulation light, which reduces power consumption and achieves a better signal/noise (S/N) ratio. The final unit will be based on the OSL (Optically Stimulated Luminescence) technique only.
- Detection unit: to detect the luminescence signal emitted after stimulation.
- Optical coupling unit: to collect the luminescence signal and transfer it to the detection unit, as well as to filter the signal from excitation and background.
- Irradiation unit: to calibrate the sample with a known dose of radiation to estimate the dose.
- Processing Electronics and Algorithms: investigating ways to calculate the age of sediments investigated and minimize the data transfer.

The project will also address redundancy components, qualification status concepts for space use of technology.

The goal of the project is the design and development of a versatile and accurate instrument with characteristics of the order of a 2 kg mass, a 2 W power consumption, a (L x W x H) size of 15 cm x 15 cm x 20 cm for on-site analysis field measurements. The project aims to put in place a product innovation by tuning and improvement of existing technologies. The preliminary design of LUMINO is based on a lens optical coupling system, a photomultiplier as the photodetector, and LEDs as the sample excitation sources. All these instruments elements will undergo a technological and operational trade-off analysis, to be optimized according to the LUMINO project requirements. For planetary exploration, as well as for Earth Science application, a portable instrument for rock and sediment dating has never been developed; however, laboratory-size equipment for Earth application exists. The expected TRL of the functional prototype is expected to be TRL 5 at the end of the project.

### **Reflectance spectroscopy of ammoniated phyllosilicates**

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#### Keywords: Ceres, Infrared spectra, phyllosilicates.

On Earth, nitrogen is present in any geological environment containing organic matter but, it is present also in igneous and metamorphic rocks as ammonium ion in a few ppm. The presence of nitrogen has been suggested on Mars soil, on comets, and in some chondrites. Ammonium-bearing minerals have been detected on the surface of (1) Ceres by the VIR spectrometer (De Sanctis et al., 2010) on-board the Dawn spacecraft. In this case, spectroscopic observations in the range of 1-5  $\mu$ m indicated the presence of NH<sub>2</sub>-phyllosilicates on the Ceres surface (De Sanctis et al., 2015). Ammonium bearing phyllosilicates can be formed by ionic exchange (Borden & Giese 2001). In this study, we describe an attempt of laboratory production and IR spectroscopic measurements of a suite of  $NH_4$ -phyllosilicates starting from the corresponding  $NH_4$ -free minerals. For each mineral we prepared three types of powder samples: raw (R), ammoniated (A), and leached (L). All samples have been spectrally characterized by means of visible/infrared spectroscopy in the INAF-IAPS laboratories with the FieldSpec Pro in the 0.35-2.5 µm range, and with the FT-IR, using a Vertex 80 spectrometer operating in the range of 2 to 14  $\mu$ m. The samples were also measured with SPIM (De Angelis et al., 2015) an imaging spectrometer operating in the spectral range  $0.2-5.1 \,\mu$ m, which is a replica of the VIR spectrometer. Reflectance spectra of the ammoniated clays show bands near 1.56, 2.05, 2.12, 3.06, 3.25, 3.55, 4.2, 5.7 and 7 µm (Bishop et al., 2002) that are related to the presence of nitrogen complex (Bruno & Svoronos 1989). The obtained results show that the various types of phyllosilicates respond differently to ammonium treatment. The  $NH_4^+$ ion can replace other ions with a similar radius inside the crystalline structure of a mineral via isomorphic replacement, thus only specific phyllosilicates are easy to ammoniate. Among the various minerals used in this study, surely the smectites were those that better accept the  $NH_4^+$  ion in their structure. On the contrary, minerals like serpentine and biotite do not show any absorption band linked to the ammonium.

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# Bedrock layering revealed by hollows on Mercury

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Keywords: Mercury (planet), layering, hollows.

The MDIS instrument, on-board the NASA MESSENGER spacecraft, provided ~26,000 images at a resolution better than 10 m/pixel by the Narrow Angle Camera (NAC). Such high-resolution images (HR-NAC) are key to uncover the morphology, texture and structure of the Hermean surface. However, Mercury's regolith does not permit to look at the pristine bedrock. The areas where exposed bedrock is most likely detected are usually located on steep scarps, such as crater walls, or crater central peaks and peak rings, where mass wasting processes cause regolith removal. In particular, crater central peaks often reveal the sub-surface lithology that was uplifted, tilted and strained by the impact process. Moreover, on Mercury, regolith removal might occur also via hollows formation, which are supposed to form because of a process of sublimation or volatile loss (Blewett et al., 2013). In order to find the bedrock exposures, we checked all HR-NAC that captured the locations of interest with particular attention to those craters that also encompass hollows. Nonetheless, chances of finding such evidence are very low because of the scarce coverage of such high-resolution images that need to capture both peaks and hollows. We verified that only few tens of these show a texture that could seemingly be related to bedrock exposure. However, three peak-related HR-NAC frames surprisingly revealed evidence of putative layered and uplifted mega-blocks outcropping on the floor of some hundredsmeters wide hollows. Although it is quite common to observe tilted layered blocks in correspondence of crater uplifts on Earth and Mars (e.g., Caudill et al., 2012; Kenkmann et al., 2014), it was never observed on Mercury before. In particular, we estimate an almost constant layer width of 10-16 m. Observing such features implies the existence of a layered bedrock before the crater formed. No evidence of layering at this scale was provided for Mercury so far. However, it is possible that the surface's widespread lava flows have undergone a layering process, whether a) several flow events occurred causing bedding discontinuities, or b) the wide cycle of temperature changes at the surface might have caused runny flows during daytime and inflation during nightime. We aim at repeating the measurements also on other similar features found elsewhere on Mercury to better constrain their origin.

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# The 1908 Tunguska Event

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Keywords: 1908 Tunguska Event, extraterrestrial bodies, Lake Cheko.

The so-called Tunguska Event (TE), of June 30 1908, is one of those phenomena that have generated a great and durable interest into generations of earth and planetary scientists and a worldwide audience. This is due to several causes, including the remoteness of the site where it occurred and the global scale of its effects. Thousands of kms from the epicenter, over Russia and the Northern Europe, the TE was perceived as a series of unusual phenomena, such as seismic and pressure waves and a bright luminescence in the night skies. Only several years later, in 1927, Leonid Kulik reached the explosion site, a remote region of Central Siberia close to the river *Podkamennaya Tunguska*. Kulik identified the epicenter of the explosion in a heavily forested area from the radial distribution of flattened trees, and reached the conclusion that he had discovered the remains of a large impact crater hidden by a swamp, and a number of secondary bowl-shaped holes of different sizes covered by peat bogs. This pattern, could have been caused by an asteroid that fell in a swarm of separate fragments. However, all attempts at finding macro-remnants of the cosmic body by digging these circular depressions were unsuccessful, and the hypothesis of an impact with the ground was abandoned. Subsequent expeditions have been devoted mainly to the study of the tree patterns in the devastated taiga and to the search for micro particles of the cosmic body, under the assumption that it exploded in the atmosphere.

After more than a century, the TE is far from being completely understood, although it has been the object of several studies. The most probable hypothesis is that it was caused by the impact with the Earth of a cosmic body, a comet or an asteroid, which exploded about 5-10 km above the ground, releasing in the atmosphere 10-15 Mtons of energy. However, fragments of the impacting Tunguska Cosmic Body (TCB) have never been found, and its nature is still a matter of debate.

Geophysical and geological data collected from a small lake about 8 km NNW of the inferred TE epicenter suggest that it is probably a crater left by the impact of a large TCB fragment. Evidence supporting this interpretation include its funnel-like bottom morphology, revealed by high-resolution bathymetry, and the structure and composition of sedimentary deposits below the lake floor, studied through acoustic imagery and direct sampling. Seismic reflection profiles collected from the lake show a density/P-wave velocity anomaly located about 10 m below its bottom, probably the effect of a buried object, which could have created the lake's depression, or a density anomaly caused by overpressure due to the impact. A magnetic anomaly also marks the presence of such feature.

If Lake Cheko, as much evidence seems to suggest (Gasperini, 2015), was formed as a consequence of an extraterrestrial impact, it opens the problem of recognizing impact related features on a composite target such as the Earth surface, very different from the Moon and the other terrestrial planets of the Solar System, where the morphology of "typical" impact features has been mostly studied.

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# Geological mapping of the Kuiper (H06) quadrangle of Mercury: Status update

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Keywords: planetary geology, Mercury geologic mapping.

Kuiper quadrangle (H06) is located at the equatorial zone of Mercury and encompasses the area between longitudes 288°E - 360°E and latitudes 22.5°N - 22.5°S. The quadrangle was previously mapped for its most part by De Hon et al. (1981) that, using Mariner10 data, produced a final 1:5M scale map of the area. In this work we present the preliminary results of a more detailed geological map (1:3M scale) of the Kuiper quadrangle that we compiled using the higher resolution MESSENGER data.

The main basemap used for the mapping is the MDIS (Mercury Dual Imaging System) 166 m/pixel BDR (map-projected Basemap reduced Data Record) mosaic. Additional datasets were also taken into account, such as DLR stereo-DEM of the region (Preusker et al., 2017), global mosaics with high-incidence illumination from the east and west (Chabot et al., 2016), and MDIS global color mosaic (Denevi et al., 2016). The preliminary geological map shows that the the western and norther part of quadrangle are characterized by a prevalence of crater materials which were distinguished into three classes, on the basis of their degradation degree (Galluzzi et al., 2016). Different plain units were also identified and classified as: (i) intercrater plains, (ii) intermediate plains, and (iii) smooth plains. Finally, several structures were mapped all over the quadrangle. Most of these features are represented by thrusts, some of which appear to form systematic alignments. In particular, two main thrust systems have been identified: i) "Thakur" system, with a NNE-SSW trend and a length of 1500 km, and ii) "*Victoria system*" which encompasses faults with a prevalent N-S trend, for a total length of 3500 km. Once the mapping activity is accomplished, the geological map will be merged with the other mapped quadrangles and integrated into the global 1:3M geological map of Mercury (Galluzzi et al., 2018), which is being prepared in support to BepiColombo mission.

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### Structural setting of the north-eastern sector of the Caloris basin, Shakespeare Quadrangle (H03), Mercury

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Keywords: Mercury planet, Shakespeare Quadrangle, Caloris Basin.

In preparation of the forthcoming ESA/JAXA BepiColombo mission, a 1:3M-scale geologic map of the H03 Shakespeare quadrangle of Mercury (Guzzetta et al., 2017) has been compiled by using the MDIS (Mercury Dual Imaging System) images acquired by the NASA MESSENGER mission during 2008-2015. The images revealed a moderately cratered surface of the planet, characterized by the occurrence of three main type of plains materials and several compressive tectonic structures that reflect crustal shortening, generally thought as the result of the planet global contraction.

The structures mainly occur in the western sector of the H03 quadrangle nearby the Caloris basin, the largest impact crater on Mercury and the most prominent geo-morphological feature within H03. In the north-eastern sector adjacent to Caloris, the structures, generally interpreted as thrusts or wrinkle ridges (Watters & Nimmo, 2010), have been gathered according to the scarp shape, i.e. linear or arcuate. Azimuthal analysis shows two preferential orientations for these structures. The main trend of linear structures is N40°-45°E, whereas the arcuate structures are mainly aligned along the N5°-10°E. In order to understand the possible interaction between this set of structures and the Caloris formation the "buffered crater-counting" technique (Tanaka, 1982) has been performed to derive the age of the structures using structure-superimposed impact craters density. Using the Le Feuvre and Wieczorek (2011) production function (for porous materials), both type of structures have a relative age of 3.7 or 3.6 Ga depending on the distance (1r or 2r) between the considered craters in the count and the reference structure.

The adopted technique improves the accuracy of dating with respect to the classical methods based on stratigraphic and cross-cutting relationships between structures and adjacent geologic units. Understanding the local deformation pattern and timing of faulting can significantly improve the knowledge of the past stress state of the planet.

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### Preliminary geologic map of the Beethoven Quadrangle (H07), Mercury

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Keywords: Planetary geology, Mercury, Geological mapping.

Today, a global series of 1:3M-scale maps of Mercury is being prepared in support to the ESA/JAXA BepiColombo mission, in order to set up the context for mission operations and help re-define the mission goals. In this contest, MESSENGER images are used to compile a new 1:3M-scale geological map of the H07 Beethoven Quadrangle, which covers an area of  $\sim 6M \text{ km}^2$  (7,7% of the total planet surface) at equatorial latitude. The mapping has been performed within a GIS environment and operated on a georeferenced monochromatic basemap at 166 m/pixel resolution (BDR, map-projected Basemap reduce Data Record). Additionally, the available Mercury Laser Altimeter (MLA) DTMs and the MDR (MDIS, Mercury Dual Imaging System 8-color) basemaps are used. The planet surface is characterized by impact craters, tectonic landforms and several plains deposits classified as smooth, intermediate, and intercrater plains materials (Schaber & McCauley, 1980). Craters with D > 20 km and their related materials are distinguished into three morpho-stratigraphic classes (from c1 to c3) according to their overlapping relationships. Based on the dominant contractional features affecting Mercury's (Byrne et al., 2014), tectonics structures have been interpreted as thrusts, when they show a relevant break in slope, or mapped as wrinkle ridges when break is less evident and they occur within smooth plains materials and basins. The SW sector of the quadrangle is occupied by half of the Beethoven basin, one of the largest ( $D \sim 630$  km) basin on Mercury of the late Tolstoian period (3.9 Ga). Similarly to the Caloris basin, its floor is covered by volcanic smooth plains materials and its ejecta have been mapped as Brm (Beethoven rim materials), defined as the hilly and radially lineated material, extending outside of the rim of the basin. Spectral reflectance of the surface, was also used in support of mapping, which also allowed to map low albedo sectors (blue range) as Low Reflectance Materials (LRM) and higher reflectance areas (red range) as pyroclastic materials.

The new geologic map represents a more detailed cartographic product with respect to the previously released 1:5M map of the quadrangle (King & Scott, 1990) and will contribute to improve our knowledge of the planet's stratigraphy and surface history.

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### Martian meteorites as a probe for the evolution of Mars

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Keywords: Mars, Martian meteorites, Planetary Evolution.

Martian meteorites are the only geological samples from Mars that are available for study on Earth. Most of them are volcanic rocks, and the most abundant types are the shergottites (basalts), nakhlites (clinopyroxenites), and chassignites (olivine cumulates). Mars is characterised by a stagnant-lid geodynamic regime, without evidence of homogenization of the mantle after the end of the last magma ocean phase (~4.5 billion years ago). These samples therefore carry invaluable information about the evolution of Mars' interior, as well as the planet's surface, atmosphere, and possibly also its hydrosphere..

In this work, we have determined Re-Os isotope and highly siderophile elements (HSE) abundance systematics for three meteorites from the nakhlite group (Nakhla, Lafayette, Miller Range 090136) in order to constrain the geochemical diversity of the Martian mantle and crust. Sulphur isotope data were also acquired for these nakhlites to compare with data from Gale Crater obtained by NASA's Curiosity Rover, as well as to assess a model of multiple lava flows and their relation to volcanic outgassing and the evolution of Mars' atmosphere. Additionally, these data are useful in constraining possible open-system processes of assimilation during nakhlite crystallisation.

Further to our work on nakhlites, the shergottite Tissint was analysed in order to obtain chemical information on Martian magmas and their mantle source regions, including the volatile abundance (Cl, F,  $H_2O$ ), and physical parameters such as the temperature and viscosity. Two anomalously large (~2 mm) olivine antecrysts were identified in Tissint. The cores of these olivine grains, in equilibrium with a melt, were used as geothermometers to estimate the temperature of the mantle at the time of Tissint's eruption. Olivine-liquid thermometry calculations reported a Martian mantle potential temperature of ~1600°C at ~570 Ma. Several amphiboles have also been found in Tissint. Preliminary data shows that they are Cl-F-poor amphiboles, meaning they may come from the Martian interior carrying a modest amount of water.

Combined, these results have implications for the formation and evolution of Mars, as well for the thermal state, internal composition, volcanic degassing, processes of volatile transfer, and atmospheric evolution on terrestrial planets with a stagnant-lid regime.

### An X-Rays tomographer (Tomox ) for in situ planetary exploration

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Keywords: planetary exploration, XRD, XRF, tomography.

The TOMOX instrument has been selected under the ASI DC-EOS-2014-309 call. The TOMOX objective is to acquire both X-ray fluorescence and diffraction measurements from a sample in order to: a) achieve its chemical and mineralogical composition; b) reconstruct a 3D tomography of the sample exposed surface; c) give hints regarding the sample age. Nevertheless, this technique has applicability in several disciplines other than planetary geology, especially archaeology. The word 'tomography' is nowadays used for many 3D imaging methods, not just for those based on radiographic projections, but also for a wider range of techniques that yield 3D images. Fluorescence tomography is based on the signal produced on an energysensitive detector, generally placed in the horizontal plane at some angle with respect to the incident beam caused by photons coming from fluorescence emission. So far, a number of setups have been designed in order to acquire X-rays fluorescence tomograms of several different sample types. The proposed instrument is based on the MARS-XRD heritage, an ultra miniaturised XRD and XRF instrument developed for the ESA ExoMars mission. The general idea of TOMOX is to distribute both sources and detectors along a moving hemispherical support around the target sample. As a result, both sources move integrally with the detectors while the sample is observed from a fixed position, thus preserving the geometry of observation. In that way, the whole sample surface is imagined and XRD and XRF measurements are acquired continuously along all the scans. We irradiate the target sample with X-rays emitted from <sup>55</sup>Fe and <sup>109</sup>Cd radioactive sources. <sup>55</sup>Fe and <sup>109</sup>Cd radioisotopes are commonly used as X-ray sources for analysis of metals in soils and rocks. The excitation energies of <sup>55</sup>Fe and <sup>109</sup>Cd are 5.9 keV, and 22.1 and 87.9 keV, respectively. Therefore, the elemental analysis ranges are Al to Mn with K lines excited with <sup>55</sup>Fe; Ca to Rh, with K lines excited with <sup>109</sup>Cd. <sup>55</sup>Fe will be primarily dedicated to XRD measurements, as it has been already tested for the MARS-XRD development. <sup>109</sup>Cd will be used to reinforce the efficiency of <sup>55</sup>Fe source in the production of fluorescent X-rays generated in the sample as a consequence of irradiation and to extend the analytical range of elements. Two different detectors will be used in order to increase the total amount of events collected and allow the spatial distribution of events to be recorded as well. The detectors we plan to use are SDD (Silicon Drift Detector) and stand-alone CCD (Coupled Charge Detector). SDD has higher count rate and stability and has been successfully used for XRF applications. CCD is able to record the spatial position of each event of X-ray emission, together with its energy. Therefore, we plan to dedicate this detector to XRD measurements, where the spatial position of the event is directly correlated to the type of crystal through the Bragg's law. So far, the SDD has been tested while the full prototype will be completed soon.

### Vents, faults and fractures spatial distribution: a planetary geology perspective

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Keywords: Planetary surface, volcanism, tectonics.

On Earth, structures reflecting endogenous processes, such as magmatism, tectonics and mud volcanism (i.e., vents, fractures and faults), have been analysed in term of their fractal (self-similar) clustering providing clues on the depth of the fluid source or on the thickness of the fractured mechanical layer (Bonnet et al., 2001; Mazzarini & Isola, 2010; Mazzarini et al. 2013; Soliva & Schultz, 2008). Planetary geology mostly uses remote sensing data sets (spectral, topographic and geophysical) and insights into the lithospheric structure at depth relies on the analysis of geological features such as fault, fractures, vents and craters that decorate rocky (icy) planets' surfaces. Self-similar clustering analysis of geologic features has been successfully applied to the study of large shield volcano (Pozzobon et al., 2015) on Mars and on fracture network in icy Enceladus satellite (Lucchetti et al., 2017). After an introduction to the method we show an application of this methodology to the study of a volcanic field in the Tharsis province on Mars (Bleacher et al., 2009) and will discuss the obtained results.

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### Diamond formation in ureilites: a shock origin inferred from diamond in Almahata Sitta ureilites

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Keywords: diamond, ureiltes, Almahata Sitta.

Almahata Sitta is the first meteorite originated from a known asteroid, since its asteroidal parent body, the asteroid 2008 TC<sub>3</sub>, was discovered and tracked a few hours before it hit Earth. As its photometric data and reflectance spectrum were collected, Almahata Sitta is also the first meteorite observed to derive from a spectrally classified asteroid (Jennisken et al., 2009). Almahata Sitta fragments show a great lithological diversity, so that the meteorite is classified as a breccia (Bischoff et al., 2010). Diamonds, common in ureilites, were reported in the first studied fragment and were characterized using Raman spectroscopy (Ross et al., 2011). Later, Miyahara et al. (2015) studied diamonds in another fragment and hypothesized the presence of large single crystals. In the same fragment, Nabiei et al. (2018) reported the presence of chromite, phosphate, and (Fe,Ni)-sulfide inclusions embedded in diamond. The authors suggested that the composition and morphology of the inclusions infer a formation pressure higher than 20 GPa, and thus a Mercury-size parent body. We analysed diamonds from the fragments 209B and 72 from the Almahata Sitta meteorite. X-ray diffraction measurements show that all samples are large polycrystalline aggregates of diamond, graphite, metallic iron and iron sulphides. The presence of the hexagonal polymorph of diamond, "lonsdaleite", was also detected, implying the occurrence of impact and/or shock events, in contradiction to the conclusion of Nabiei et al. (2018).

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### Fine-grained Antarctic micrometeorites and weathered carbonaceous chondrites as possible analogues of Ceres surface

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Keywords: Ceres, Meteorites, Metasomatism.

Ceres is an icy body with surface composition close to the carbonaceous chondrites (CCs) (McCord & Zambon, 2018). No analogues in the meteorite collections have been found yet. For this reason we analysed CCs that suffered strong weathering in Antarctica (AWCCs), possibly the closest terrestrial environment to Ceres surface, and fine-grained micrometeorites (MMs) since might represent C-asteroid regolith (Suttle et al., 2017). In particular, the analysed 5 MMs (5.29, 18c.11, 19b.7, 6.14 and 18c.13) show NIR spectra close to the average NIR spectra of Ceres. MMs 5.29 and 18c.11 are dominated by Fe-rich olivine, Ca-Fe pyroxenes plus andradite, jarosite and minor phyllosilicates. MMs 19b.7, 6.14 and 18c.13 are more weathered and major phases are jarosite and Fe-K sulfides. Among the AWCCs we found the CM2 meteorite GRA98005 that had one side exposed to the Antarctic environment and one side with pristine composition. Spectra on the pristine side are featureless while spectra of the weathered side are close to Ceres spectra. On the weathered side GRA98005 is dominated by Fe-oxides, gypsum, enstatite, forsterite and minor carbonates. All these features suggest that MMs 5.29 and 18c.11 are the result of aqueous alteration at T<300°C (Krot et al., 1998), while the other MMs and GRA98005 show a composition that is the result of rock-ice interaction (Lee & Bland, 2004).

We propose that MMs 5.29 and 18c.11 might represent products of Fe-alkali-halogen metasomatism that started from the interior of Ceres and expanded close to the surface (Castillo-Rogez & McCord, 2010). MMs 19b.7, 6.14 and 18c.13 and GRA 98005 are instead representatives of the crust of Ceres that suffered minor hydrothermal activity and underwent a process similar to the Antarctic weathering. This is in agreement with a layered subsurface material (McCord & Zambon, 2018). Furthermore we might also assume that impacts that exposed the subsurface layers of Ceres created a mixture on the surface, which is consequently made up of chunks of the upper crust and underlying metasomatized layers.

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### In-situ dating of recent sediments on the surfaces of Mars and the Earth

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### Keywords: Planetary surfaces, dating, luminescence.

The geological and climatic evolution of Mars has been different from that of the Earth. Early Mars deposits show remarkable similarities with the Earth as for rivers, lakes and related features. Glacial deposits are extensive as well as are polar caps. The Noachian era was likely dominated by Earth-like landscapes with an abundance of water. Climate deterioration occurred at the threshold between Noachian and Hesperian with a likely loss of atmosphere and decrease of water, resulting in a dry environment. However, the Hesperian and Amazonian dry setting was punctuated by short (no idea of the duration) periods with large amounts of water. Nothing is known about the most recent (the last million years) history. Morphological evidences suggest that water was not present on the surface, apart from some small and localized waterflows such us gullies and grain flows, covered by extensive aeolian deposits. Recently aeolian deposits and gullies have been observed to be active at present time. Unfortunately, there is no possibility to date these deposits even with the highest-resolution crater counting. We may, however take advantage of in-situ analysis.

To constrain younger ages, either samples returned to Earth for analysis are required, or in situ techniques for obtaining absolute dates of surfaces and geomorphologic features need to be used. Establishing a chronology for surface-shaping events is essential to interpret geological, geomorphologic and climatic history. Mars sedimentary deposits may serve as "Rosetta Stone" for understanding the recent geologic and climatic history, by documenting variations in volatile mass balance, insolation, atmospheric composition, dust storm activity, volcanic eruptions, large impacts, catastrophic floods, and possibly records of putative extinct or extant life.

We consider the unique challenges presented by the Martian surface and discuss the various concepts and the possibilities offered by luminescence techniques for the design of a low-power, low-weight instrument for in-situ measurements as a part of the payload of Martian landers and rovers. The radiation exposure can be measured by stimulating a sample with heat or light and monitoring the emitted luminescence, the intensity of which is a function of the total radiation from the environment in the time elapsed since the last resetting event. If the rate of natural irradiation is constant and can be determined, then dividing the absorbed dose by the dose rate gives a radiation exposure age. Ways to determine dose-rates on Mars are addressed.

These topics are being addressed by the LUMINO project, about the technological and economic viability of a leading-edge instrument for dating Mars samples: a miniaturized instrument for in-situ analysis and assessment based on luminescence methods. In addition to planetary applications, LUMINO also addresses terrestrial field applications as a light and portable dating instrument in geology and archaeology surveys.

### PRISMA and GHIBLI: from meteors monitoring to simulation of entering the atmosphere

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### Keywords: PRISMA, GHIBLI, meteorites.

The PRISMA (Prima Rete Italiana per la Sorveglianza di Meteore e dell'Atmosfera) project involves the creation of an Italian network of all-sky camera for the observation of very bright meteors (the so-called bolides and fireballs), in order to determine the orbits of the objects that cause them and delimit with a good degree of approximation the areas of any fall of fragments to recover meteorites. A similar network has been developed in France in the project FRIPON (Fireball Recovery and InterPlanetary Observation Network).

Researchers from the National Institute of Astrophysics (INAF) and Universities as well as amateur astronomer groups and regional and local Astronomical and Meteorological Observatories participate the PRISMA project. Schools are also involved with an educational program and with astronomy workshops that aim to engage students, teachers and individual citizens in the research activities of the project, side by side with researchers.

The networks like PRISMA and FRIPON are of great interest for the studies of interplanetary bodies and the dynamical and physical evolution of the population of very small bodies of the Solar System and for the studies of meteorites falls. Those eventually recovered will be classified and investigated from the petrologic, genetic and evolutionary points of view (Grady et al., 2014).

A further step in PRISMA project could be represented by the possibility to observe the spectral features of meteorites entering the atmosphere. Some observations have been already performed by Vojáček et al. (2015) and the spectra have been classified according to relative intensities of the emission lines of Mg, Na, and Fe.

The phenomena of meteorites entering the atmosphere, although frequent, are not enough to perform experiments that allow us to understand what really happens, also because of the short time of interaction and the difficulty in grasping the phenomenon.

For these reasons it was decided to carry out laboratory experiments simulating the conditions for the entry of meteorites into the atmosphere in the GHIBLI hypersonic tunnel at the Italian Aerospace Research Centre (CIRA). In particular, meteorites samples were exposed to hypersonic flows of plasma composed of air and argon to achieve the typical heating conditions of the entry into the atmosphere and perform imaging experiments in the visible and infrared. Moreover, these simulations allow to verify the morphological and thermal dynamics of the interaction process and to perform spectroscopy experiments in order to collect the emission spectrum of the radiation emitted in the process.

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### A multidisciplinary approach to the study of the Chaotic Terrains on Mars

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Keywords: Chaotic Terrains, Mars, Numerical Modeling.

Chaotic terrains on Mars display common characteristics, such as irregular arrays of fractured and tilted blocks up to tens of kilometers in size and their occurrence in depressions of hundreds of meters deep. Moreover, they represent the source of the majority of the Hesperian outflow channels. These features spark the question which subsurface mechanism is responsible for the formation of chaotic terrains and release of major quantities of water in few. Morphological and hydrological observations fit well with a scenario of catastrophic water release from a buried sub-ice lake. In this scenario, the Chaotic Terrains would result from the collapse of sediments and ice covering the lake. The sub-ice lake would arise from slow melting of, and sedimentation on, a crater ice sheet. In order to investigate whether this scenario is feasible from a physical perspective, we perform a multidisciplinary study of the Chaotic Terrains. In particular, we perform a statistical analysis of their morphometric characteristics, and we investigate whether their surface morphology may be a consequence of the collapse of the infill of a crater.

Based on their morphometric characteristics, we find that these landforms have a common origin. In particular, the investigated landforms show diameter-depth correlations similar to those that impact craters of equivalent diameters exhibit. We also find that the observed amount of collapse of the collected features is strongly correlated to their diameter. Furthermore, the linear relation between the minimum filling and pristine depth of craters, the constant ratio between collapse and the amount of filling and the fractured and chaotic aspect of the filling agree with melting and subsequent collapse of an ice layer below a sediment layer.

We investigate whether this surface morphology may be a consequence of the collapse of the infill of a crater. We perform numerical simulations to evaluate the distribution of fractures within the crater and the influence of the crater size, infill thickness, and collapsing depth on the final morphology. The comparison between model predictions and the morphology of the Martian Chaotic Terrains shows strong statistical similarities in terms of both number of fractures and correlation between fractures and crater diameters. No or very weak correlation is observed between fractures and the infill thickness or collapsing depth. The strong correspondence between model results and observations suggests that the collapse of an infill layer within a crater is a viable mechanism for the peculiar morphology of the Martian Chaotic Terrains.

## From Earth to Mars: mineralogical and geochemical perspective from NASA's rovers and from a recent discovery in the Aeolian Arc, Sicily

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Keywords: Mars, iron-ooids, hydrothermal activity.

In the last decades, the Martian NASA's rovers produced an enormous amount of data, in the terms of high-resolution images, chemical and mineralogical composition of the martian soils and rocks. Interesting for mineralogists and geochemists are the Mössbauer data acquired by Spirit and Opportunity, and XRDP carried out by Curiosity. In addition, all the rovers are equipped with an APXS instrument (Alpha-Particle X-Ray Spectrometer) for bulk analysis and a microscopic imaging camera.

The collected data re-reading, however, highlights some anomalies. Pyroxenes, olivines and magnetite represent the most diffuse mineral phases besides hematite, goethite and nanophase oxyhydroxides. The average sulfur content in rocks and soils, in the range of 7 %, can reach the remarkable value of 40 %. Most of the identified mineral phases could be closely associated to hydrothermalism. In addition, spherical particles similar in composition to terrestrial ooids have been photographed by all the rovers in some of the detected areas such as Gale Crater (Curiosity), Meridiani Planum (Opportunity) and Gusev Crater (Spirit). For instance, at Meridiani Planum crossed by Opportunity Rover, the soil appears discontinuously covered by iron-rich spherules resembling iron ooids.

Here we report, the wide iron-ooids deposit recently discovered off Panarea Island, located on an active submarine hydrothermal system recognised as the responsible for their formation. Emphasis is placed on linking geometric properties to physical mechanisms. The recent terrestrial iron-ooids are millimetre-concentric depositions of primary cryptocrystalline goethite on pre-existing sediment/skeletal particles. Hydrothermal fluids composed of a mixture of thermal waters and  $CO_2$ -dominated gases vented through the seafloor sediments acted as supplier of iron and builders of the laminated structure due to agitation of loose sediment particles.

In this scenario, we provide new insights into the origin of the spherical-grains-bearing deposits of Mars for which several genetic hypotheses (including those involving biological activities) have been proposed. The exceptional recently iron ooid deposit discovered in the SE Tyrrhenian Sea, represents an excellent natural laboratory to relate a hydrothermal system and vents, that on Mars might have harboured life, with structures and mineral compositions that on the surface of Mars seem to be widespread.

# Distribution, stratigraphy, and layer thicknesses of intra-crater deposits in Western Arabia Terra, Mars

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Keywords: Mars, Sedimentology, Deposition.

Arabia Terra is a regional dichotomy boundary between the high and lowlands of northern Mars known for its densely cratered terrain and extensive distribution of water-altered deposits. By analyzing the intra-crater deposits' stratigraphy and mineralogy, as well as surveying their geographical distribution, sedimentary facies across the region can be compared. 1013 craters were observed within a 2,000 by 3,100 km area of western Arabia Terra, bounded by the Oxia Palus quadrangle (MC-11), with the aim to identify and characterize potential water-altered deposits. Several distinct varieties of deposits were found and distinguished by their mineralogy, albedo, thermal-inertia, layering, and erosional landforms. In general, deposits appear either as a thin veneer or a bulky mass that is commonly layered. Veneer deposits were observed in 22 craters and bulk deposits were observed in 55 craters. Geographic relationships between the distribution of intra-crater deposits and areas of extensive plateau deposits, particularly around Mawrth Vallis and Meridiani Planum, suggests multiple upwelling sources of varying depth and intensity at different intervals. Veneer deposits into craters. A scenario involving a complicated multi-depositional environment of upwelling groundwater, the drainage of plateau surface water, and aeolian processes is proposed for the depositional history of Arabia Terra.

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# Emissivity and reflectance spectra of sulfide-bearing samples: new constraints for the hermean surface composition

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Keywords: Mercury surface, reflectance spectroscopy, emissivity.

Mercury is an extreme planet, the smallest, the closest to the Sun, and the planet with the largest temperature excursion in the Solar System, from ca. -180°C to ca. 430°C. This high temperature range may affect spectral properties of the surface.

Recent studies concluded that the hermean surface is Mg-richer and Al, Ca and Fe-poorer than Moon and Earth and enriched in volatiles and alkalis as (Braden and Robinson, 2013). Vander Kaaden et al. (2017) constrained the potential mineralogy of Mercury's surface as dominated by plagioclase, pyroxene, olivine, with lesser amounts of quartz, and with compositions varying from alkali-rich komatiites to boninites. Furthermore, some peculiar mineralogical assemblages were suggested, like the presence of abundant sulfides in hollows (Vilas et al., 2016).

A detailed literature about the spectral behavior of mixtures composed with hermean-like minerals (e.g., sulfides) under different temperature conditions still lacks.

We thus measured the reflectance spectra in VIS\_MIR range (0.4-16  $\mu$ m) and the emissivity of size-intimate mixtures of different end-members at PSL (Planetary Spectroscopy Laboratory) at DLR, Berlin.

We select 2 end-members: 1) a Mg-rich gabbronorite sample and 2) a Ca-sulfide, both at a fine grain size (<63  $\mu$ m). Starting from these end-members, mixtures are prepared, with increasing sulfide abundances% (80, 60 and 40%, respectively). Emissivity spectra were acquired at four different temperature, 100°C, 200°C, 300°C and 400°C; reflectance spectra (i=13°; e=17°, 0.8mbar) were acquired from both fresh and heated samples.

Preliminary results show how the heating process produces a reflectance increase and a spectral contrast decrease in the VIS range, and the appearance of new structures in the MIR. Spectral features are affected by the temperature also in the emissivity spectra.

These mixtures are important to understand the influences of different amounts of sulphide on spectra from hermean regolith.

Our work will help to define indicators useful to analyze remote sensed data and will contribute to the creation of a spectral library to which compare results from orbit.

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# Melting Temperature of Tagish Lake (CI2) meteorite from 5 to 30 GPa: implications for the fate of the Carbonaceous Matter during planetary accretion

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Keywords: Earth's volatile budget, carbon speciation, Tagish Lake.

Current models of planets formation suggest the possibility that volatile-rich carbonaceous chondrites are carriers of water and complex carbon molecules implying their key role in the volatile budget of planet's interiors like Earth. Tagish Lake (TL) meteorite is an ungrouped C2 chondrite whose bulk and organic chemistry compositions have been carefully studied over the last decade. The mineralogy of TL meteorite consists of organic compounds and S-bearing phases such as Fe-Ni sulfide coexisting with abundant carbonate, magnetite and serpentine phases. Therefore, the knowledge of the speciation of carbonaceous matter during the history of a meteorite at extreme pressures-temperatures is of fundamental importance to understand the volatile contribution during early planetary differentiation such as the core formation as well as bulk composition and redox state of the mantle in terrestrial planets.

We performed experiments at 5, 12, 21, 25 and 30 GPa, and temperatures between 800 and 1900 °C using multi anvil apparatus. The starting material consisted of natural Tagish Lake meteorite sample permanently stored into a desiccator after being grinded. The recovered run products were polished for textural and chemical characterization of the mineral phases using FE-SEM, electron microprobe and Raman spectroscopy, respectively. Ultra-thin sections, ~100 nm thick, were prepared from the recovered samples using a focused ion beam, and then transferred to TEM grids for X-ray absorption near-edge spectroscopy (XANES) analyses of carbon using a scanning transmission X-ray microscope (STXM) at the Advanced Light Source, Lawrence Berkeley National Laboratory.

Preliminary results show the effect of volatile on the melting temperature of Tagish Lake (CI2) with respect to Allende (CV3) meteorite, enstatite chondrite and KLB1, respectively. In addition, results show the stability of the aromatic component with development of graphene structure after high temperature and pressure experiment. Results are used to derive a model of accretion that takes into consideration the stability of polymerized carbon species along with elemental carbon and carbonate either liquid or solid Fe-Ni sulfide melt. Results from this study has important implications for the evolution of the Earth's mantle redox state and the deep volatile cycle over time.

# Investigation of clay minerals in Margaritifer Region on Mars: Implication for pedogenetic processes and the ages of soils using terrestrial analogues

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### Keywords: Mars, soil, clay minerals.

Margaritifer region of Mars represent the most interesting areas where study the weathering processes, due to the strong evidence of past hydrological activity and the mineralogical composition including clay minerals suggesting a prominent exobiological potential. Furthermore, previous works of dating the ages of Margaritifer soil is quite poor. We purpose to reconstruct the processes formation of clay minerals and the age in soils exposed in the Margaritifer regions using the comparison with Etna and Cerviero soil analogues and reproducing the weathering processes experimentally in the laboratory respectively. We use a multidisciplinary approach coupled mineralogical qualitative (CRISM analysis) and quantitative (MESMA tool) analysis for Mars and pedological, mineralogical and chemical analysis for the terrestrial analogues. CRISM data show clavs widely exposed in Margaritifer region on Mars, where we detected allophane as well as vermiculite, chlorite and smectite. We find good analogies between Etna volcano and Cerviero mount choose, as terrestrial soil profiles analogues and the Martian terrains, in terms of bedrock composition and clay mineralogy. We associate the different clay minerals formation to chemical weathering alteration and hydrotermal alteration. The experimental alteration performed in the laboratory on alkaline Etnean basalts suggests that acidic conditions (pH values ranged between 3.5 and 5.0) and temperature ranged between 150°C and 175°C and acidic promote the clay neoformation. Therefore, we can hypothesize that in Margaritifer regions, the acidic conditions in a warm humid climate similar to the Mediterranean area on the Earth, may have been responsible for the clay formations, accelerating the time of formation. The amount of clays closes to 50-60% estimated from MESMA analysis in the Margaritifer region is comparable to clay contents of red Mediterranean soils comprised between about 0.5 and 1 Ma, developed during warm and humid climatic conditions of Pleistocene interglacials (Scarciglia et al., 2015) and the red soils in the tropical environments ranged in age from about 40 ka to 200 ka (Delarmelinda et al., 2017). The iron oxides also obtained from MESMA data (ca. 11 to 16%) are in accordance with the redness rating RR estimated from the NASA rover on Mars that exhibits similar values of Mediterranean and tropical soils. Margaritifer regions on Mars show clear evidence of past water-shaped landforms as suggested by the clay mineralogy, which could have been deposited at centennial to millennial up to million-years timescales.

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Scarciglia, F., Pelle, T., Pulice, I., & Robustelli, G. (2015). A comparison of Quaternary soil chronosequences from the Ionian and Tyrrhenian coasts of Calabria, southern Italy: rates of soil development and geomorphic dynamics. Quaternary International, 376, 146-162.

### Secular variations in the Nb-Ta signature of the mantle: a window on Earth accretion

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Keywords: Nb/Ta, planetary accretion, impact.

The imbalance between the chemical composition of the silicate Earth and that of chondrites has arisen several geochemical paradoxes, which are used to model planetary accretion and better understand how Earth formed and evolved through time. Some of the key constraints on early differentiation processes assume that our proto-Earth had a bulk homogeneous subchondritic composition in the elements niobium and tantalum (also known as Nb-Ta paradox), and that no secular variation in their relative abundance occurred since accretion.

We addressed the question pertaining to the timing and origin of the Nb-Ta paradox by monitoring the secular variation of the Nb/Ta signature of primitive mantle-derived magmas emplaced in different geodynamic settings, from the Archean eon through to the Phanerozoic. Most of the calculated Nb/Ta and Zr/Hf values define a positive array that lies along a slightly lower slope (but within error) in relation to the known terrestrial array (Münker et al., 2003), intersecting the Zr/Hf chondritic value at the significantly subchondritic Nb/Ta value of  $13\pm1.6$  However, the striking aspect of our dataset is the fact that a significant number of calculated melts deviates from the main array, showing anomalously high Nb/Ta ratios even at chondritic Zr/Hf values. The anomalously Nb/Ta enriched melts are also not restricted to any specific setting or geological time, but rather occur throughout the evolution of the planet in different environments.

Here, we thus provide new evidence that mantle domains variably enriched in niobium/tantalum, even approaching the chondritic composition, exist and have been periodically sampled since early Archean times by magmas formed at depth and emplaced on the surface. These domains likely reflect re-enrichment of an originally niobium-depleted magma ocean through addition of extra-terrestrial chondritic material. We argue that the postulated enrichment process occurred during a giant impact after core formation, in a time window that coincides with the collision that is thought to have generated the Earth's Moon.

Münker, C., Pfänder, J. A., Weyer, S., Büchl, A., Klein, T. & Mezger, K. (2003): Evolution of Planetary Cores and the Earth-Moon System from Nb/Ta Systematics. Science, 301, 84-87.

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# **Session S42**

# Geosciences at school 2018: geoscience and society

Conveners AND CHAIRPERSONS Francesca Cifelli (Università di Roma Tre) Rosolino Cirrincione (Università di Catania) Eleonora Paris (Università di Camerino) Manuela Pelfini (Università di Milano) Angela Tosto (ANIS)

# "Replace fear of the unknown with curiosity": seminars on natural risks in Rome metropolitan area

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Keywords: civil protection, natural risks, Rome metropolitan area.

In the frame of its institutional duties, the Geological Survey of the *Provincia di Roma* promoted, since 2014, seminars on natural risks held for workers who, attending their duties mostly outdoor, could be potentially involved in critical scenarios. Aim of the information was disseminating the culture of awareness among civil protection operators (police officers, park rangers, volunteers, technicians of local authorities), preventing the possibility for emergency relief workers to become, instead, people to be rescued.

With the recent reform of local government in Italy, the former *Provincia* was abolished and replaced in 2015 by a new institution, the *Città Metropolitana di Roma Capitale (CMRC)*. Among its civil protection responsibilities, the new Authority promoted a program of educational seminars addressed to students and teachers of primary and secondary school concerning natural risks. For the service, performed by public officials voluntarily and besides their ordinary duties, no specific budget has been allocated.

Described activities were planned by Geological and Civil Protection Survey of *CMRC* partially in partnership with the *Università della Campania "Luigi Vanvitelli"* and the Regional Professional Association of Geologist of Latium, which in turn also started in 2015 an analogous project entitled "*Earth's secrets told by geologists*".

After the onset of the Central Apennines seismic sequence in August 2016, educational activities were concentrated on earthquakes. Although in the Rome metropolitan area no significant damage occurred, the main shocks of the sequence (2016, August 24th; October 26th and 30th; 2017, January 18th) were largely perceived throughout the whole territory, including Rome urban area. Consequently, youth having experienced directly or indirectly such natural disasters become emotively involved in such issue, rather in other events that never occurred in their lives.

Independently from the specific approach chosen for different age groups, the main goal of the project is to spread the culture of prevention, improving students' state of awareness about environmental hazards in their hometown and in the surrounding areas. In this way, youth is encouraged to become in turn messenger of good information, replacing fear of the unknown with curiosity.

# "Researchers for 1 week". A project of 'Alternanza scuola lavoro' as an example of school at Geosciences

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Keywords: students, high school, 'Alternanza scuola lavoro' project.

With the aim to link theoretical knowledge acquired in the school with practical research activity of a typical research institution of CNR, 10 students of an high schools (Istituto d'Istruzione Superiore 'Einstein-De Lorenzo') in Potenza (Basilicata) lived the experience to be 'researcher for 1 week' at Institute of Environmental Analyses - IMAA/CNR. According to the mission of the Institute, during this time, one group of them performed laboratory experiments to synthesize zeolite from pure silica and alumina sources. The other group was devoted to the mineralogical and morphological characterization of four samples of soil with the aim to investigate the geology of one specific sector of Southern Apennines.

The students were the main actors for all the activities dealing with both topics. The proposal of this project was in fact to bring them closer to different aspects of the research job, from the study of the problem to the realization of experiments. They also carried out a short seminar on the activity performed and results achieved.

With this project, the students were sensitized towards the role of the researcher and on the relevance of the research activities, in order to increase and reawaken their awareness.

# Dendrogeomorphogical reconstructions on polygenic debris fan as a tool for approaching geo-risks with students of different ages

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Keywords: Debris-flow fans, Dendrogeomorphology, Geoeducation.

Reading the landscape is a key starting point not only in acquiring knowledge in Physical geography and Geomorphology but also in taking awareness for what concerns the relationship between Earth Sciences and Society, with a particular regard towards resources and risks. Physical processes shape the landscape whose features are strictly linked with litho-, bio-, atmo- and anthroposphere. A common belief in student is the immutability of the Earth surface as well as the absence of links between landforms and what grows on them as vegetation. Anyway, the reconstructions of past geomorphic events, by means of trees, can represent one of the most involving strategy to get in touch with surface processes as agents of landscape modelling, geosites genesis and hazards source. Alluvial and debris-flow fans, debris and polygenic cones, including those fed by snow avalanches, are common features in the mountain landscape. They are generally known by students basing on personal experiences and well represent examples of mass wasting effects. According to past tested experiences (Pelfini et al., 2016), a model of educational approach, modulated for different scholar targets, is proposed, basing on results of scientific researches (Bollati et al., 2017). A sequence of educational steps has been elaborated starting from field observations and activities, simple dendrochronological and dendrogeomorphological reconstructions, interpretations of depositional landforms evolution, hazards and risks linked with modelling processes. From field evidences observed along a touristic trail in the Loana Valley (Verbano-Cusio-Ossola Province), according to the principle of *learning-by-doing*, the activities proposed to students allow to approach various topics: i) topographic map use; ii) reading of simplified versions of geomorphological maps (geomorphological boxes) for individuating areas affected, currently and in the past, by geomorphic processes; iii) applying dating methods to graphical representation of tree cores for supporting geomorphological reconstructions (dendrochronology) and to assess trees as a source of environmental data (dendrogeomorphology); v) making considerations on human interventions (defence works) for risk mitigation in mountain environments. The different testing phases, also involving researchers operating in other fields of research, have evidenced its feasibility with students of very different ages, just varying disciplinary goals, difficultly level and time at disposal for performing activities.

Pelfini, M., Bollati, I., Pellegrini, L., Zucali, M. (2016): Earth Sciences on the field: educational applications for the comprehension of landscape evolution. Rend Online Soc Geol It, 40, 56-66.

Bollati, I., Crosa Lenz, B., Zanoletti, E., Pelfini, M. (2017): Geomorphological mapping for the valorization of the alpine environment. A methodological proposal tested in the Loana Valley (Sesia Val Grande Geopark, Western Italian Alps). J Mount Sci, 14(6), 1023-1038.

### Sicily: a geological laboratory

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Keywords: school, job, museum.

"Geologists at risk of extinction": this is the opening sentence of an article of March 29, 2016 of "Il Sole 24 ORE", (1) that fits well the difficult situation that this professional category is experiencing in recent years. It has been witnessed, in fact, a strong reduction in the educational offer in both the school and university system, with the number of Departments in Earth Sciences dropped from 29 to 8, accompanied by a progressive reduction in enrollment and graduates, from 1140 in 2002 to 586 in 2008 (2). Numbers that make you think, especially if contextualized to the Italian territory, widely characterized by the hydrogeological, seismic and volcanological risk, in whose prevention the geologist plays a primary importance role. Sicily is one of the Italian regions in which we find three types of risk mentioned above and it is precisely in this context that we find the path of Alternation School-Work (ASL), "Sicily, a geological laboratory", realized in within the MAGiS project (Open Museum for Young Scientists), in 2017, thanks to the contribution of the Naturalistic Association Geode ONLUS. The project took place at the "Museum of Mineralogy" of Palermo, Department of Earth and Sea Sciences of the University of Palermo, which houses one of the richest, over 10,000 samples and ancient collections of rocks, minerals, instruments and other historical artifacts.

The proposed path had two main purposes: 1) to enhance the wealth and historical, cultural, naturalistic and scientific heritage preserved not only at the Museum of Mineralogy, but also at the collections conserved in the schools involved; 2) bring students closer to the world of university and work, particularly in the field of Earth Sciences. 45 students, aged between 15 and 18, were involved in carrying out the activities, valuing the aptitudes and skills of each of them.

With the aim of enhancing and increasing the usability of the aforementioned collections, to date below potential, young students have been provided with the tools and skills necessary for planning and conducting museum visits. The students were also trained for the organization and realization of the international event "European Night of Museums" at the Museum of Mineralogy.

To this end, students were given lectures and experiential workshops on Geology and Mineralogy in general, and on the geology of Sicily in particular. Theworkshops allowed the students to touch rocks and minerals, contextualizing them to the Sicilian territory, characterized by all the main types of rocks, as well as by important successions of minerals, studied at international level, dating back to the period known as "Messinian" (7.246 - 5.332 Ma).

- (1) <u>http://www.scuola24.ilsole24ore.com/art/universita-e-ricerca/2016-03-24/contro-crisi-italia-geologo-guarda-all-europa-194146.php?refresh\_ce=1&uuid=ACJ9LTuC.</u>
- (2) http://www.neogeo.unisi.it/galleriaimmagini/mercato\_geologi\_italia\_ok2.pdf.

### Urban Geology: field trips in the city centre to discover lithological geodiversity

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Keywords: urban geology, lithological geodiversity, GeoODK Collect App.

Outdoor activities are a powerful tool in teaching Earth Sciences. However, most secondary schools have great difficulties in organizing field trips to geological sites far from their own location for several reasons (e.g., travel distance and costs, insurances, availability of time). The project "Urban Geology" has been developed in recent years by a multidisciplinary team in the frame of the "Piano Lauree Scientifiche" (i.e., "Scientific Degree Plan", an initiative of the Ministry of Education aimed to sustain Science, Technology and Mathematics studies). The project offers to Earth Science teachers at high schools a low-cost opportunity for outdoor geological activities.

A standard itinerary is proposed in the city centre of Milan (from San Babila to Duomo along Corso Vittorio Emanuele) and it is supported by a short guide made available to the school teachers, allowing them to lead the excursion by themselves. Along the itinerary it is possible to observe a variety of rocks of different origins, used as building material: sedimentary (i.e., conglomerates, sandstones, limestones), magmatic (i.e., granites s.l., rhyolites, trachytes), metamorphic (i.e., marbles, orthogneisses). Through additional information reported in the guide on the provenance area and historical use of each lithotype through times, the teacher may extend the discussion to other topics, as, for example, environmental problems related to use of rocks and minerals as georesources, or commercial routes in the different historical periods, or architecture and art transformation through times.

The project has recently been implemented leaning on the GeoODK Collect App for Smartphone. In this framework a specific form for collecting data was set and shared with students to be applied both around Milan or in their own cities or towns. They can take pictures of rocks used for buildings or monuments or other urban occurrences, they can geolocalize the site, describe and classify the rock and add information on its provenance or other details and upload all the materials, making them available to other users. The final aim is to provide the material to students to create their own itineraries to be shared through the devoted website (https://ona.io/). One of the most significant experimentation of the methodology is in progress within the framework of the "School - Job Alternance" project in collaboration with several schools in the Lombardy area.

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### SISMO-LAB: an ASL project for the realization of an educational kit on earthquakes

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Keywords: Earthquakes, laboratory experience, dissemination of scientific knowledge.

The Alternanza Scuola-Lavoro (ASL) is considered by the Italian Ministry of Education, University and Research, an innovative teaching method which helps in consolidating the knowledge acquired at school and testing students' attitudes though practical experience. As part of the ASL projects proposed in the geological area at the University of Roma TRE, SISMO-LAB was aimed to the creation of an educational kit on earthquakes that, once completed by the students, has become property of the school.

The main objectives of the project were: the promotion of knowledge on earthquakes, the improvement of analysis and design skills and the acquisition of methodological/didactic skills in the field of dissemination of scientific culture. Thirty-five students were involved, coming from 6 different schools. The project has been divided into three phases: 1) scientific training on earthquakes with particular attention to the Italian territory and the importance of disseminating scientific culture in the territory); 2) realization of the experimental apparatus that compose the didactic kit (as for example the realization of a seismometer); 3) presentation by the students of the didactic kit. The total amount of work was quantified in 40 hours.

The experience was assessed very positively both by the students, who showed interest and involvement in the realization of the whole kit, and by their teachers who noticed an active and critical participation of their students in the various phases of project implementation. In particular, the workshop experience has attracted students for practical activities, such as the use of screwdrivers, drills, saws, welders, hot glue, etc. This positive feedback has encouraged university teachers involved to continue the project for the next school year 2018/2019.

## The Hyblean Karst Museum: a tool for communicating scientific education in the territory

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Keywords: Karst Museum, scientific education.

Scientific museums are undoubtly precious tools for communicating science and its applications. Indeed, they permit to have a "real" approach to science. For this reason in recent times, they changed from exhibition centers to cultural sites where it is possible to touch and experience instruments and natural materials. In this frame, the Hyblean Karst Museum takes into account two main aspects: from the one hand, the scientific side of observed phenomena, from the other hand, the cultural implications that are strictly connected to inhabitants and territory. As far as the scientific approach, images and texts aim to reach the educational goal. They explain the geological process, so fascinating and, nevertheless, not well understood such karst in the Hyblean territory is. Moreover, caves constitute ideal environments for endemic species. The second target refers to mankind and underground life describing the cultural evolution. In this way, the Museum is not an exhibition gallery anymore, becoming instead a narrator path of science and culture. Karst process is illustrated by taking into account all of its morphological features and its genetic aspects. Moreover, the Hyblean Mountains represent a peculiar area for both animal and vegetal species. For this reason, an important part of the museum is dedicated to ecosystem explanation and description. Finally, the karst-type territory has been since pre-historical times a favored site for human settlements, due to natural caves as well as water sources. In this meaning, its archaeological interest in quite unique.

# A geologist at school: an alternative mathematics, a geo-touristic travel forward Moon, the synonymous list of *Homo sapiens* and the poetry of Giacomo Leopardi

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### Keywords: Moon, Racism, Leopardi.

Teaching geosciences at school doesn't mean only to explain concepts of Geology but a geologist at school can indicate some alternative or uncommon approaches to common objects. Four examples follow: an alternative way to teach mathematics, a proposal for a geo-touristic travel on Moon, the synonymic list of *Homo sapiens* Linneaeus, 1758 and a study about Giacomo Leopardi and Icelandic volcano Hekla.

A project about the mathematics and geometry of nature have been realized. The Students have been bring to visit columnar basalts, to touch by hand wet or dry mud cracks, watching the shape of some fossils or crystals. Finally mathematics become real and not only theorist.

A student projected a geotouristic travel forward Moon. Even though it remains only a desire, the idea of next future sustainable tourism on our satellite seems to be interesting. Starting by motivation, passing by physical preparation until what geological beauties to see, using a selenological map (e.g. Fortezzo & Hare, 2013), a travel has been projected.

Another study regards the scientific confutation of racism. Together *Homo sapiens* Linneaus, 1758 instituted a species for every human race. Goal of the project is to put in synonymy the wrong names of human species.

The last project speaks about the citation by the italian poet and philosophers Giacomo Leopardi, about the icelandic volcano Hekla, in the *Operetta Morale* entitled "*Dialogo della Natura e di un Islandese*" (Leopardi, 1824):

"Né potea conservare quella tranquillità della vita alla quale erano rivolti i miei pensieri: perché le tempeste spaventevoli di mare e di terra e ruggiti spaventevoli del monte Ecla non intermettevano mai di turbarmi."

During studies for the primary level secondary school thesis about the works and the life of Leopardi, some questions arises up: How was it possible for Leopardi to know information about Icelandic volcanoes? and what did Hekla's eruption to become so important to be mentioned by an central Italy author?

The projects here presented are not connected with the teaching of Geology, but they start from a geological point of view and they show how a different way to speak about Geology is desirable.

Fortezzo C.M. & Hare T.M. 2013. Completed digital renovation of the 1:5000000 Lunar Geologic Map Series. 44th Lunar and Planetary Science conference, 1-2.

Leopardi G. 1824. Dialogo della Natura e di un Islandese. operette Morali.

Linnaeus C.N. 1758. Systema naturae per regna tria naturae, secundum classis, ordines, genera, species cum characteribus, differentiis, synonymis, locis. 10th ed. Vol. 1. Laurentii Salvii.

### Geological features of the Cutgana nature reserves: new educational strategies and implementations in the museum areas

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Keywords: Environmental awareness, Nature Reserves, educational strategies.

The Cutgana (Centro Universitario per la Tutela e Gestione degli Ambienti Naturali e degli Agro-Ecosistemi) is a multidisciplinary Research Center of the University of Catania.

In collaboration with numerous national and international scientific institutions, the Cutgana promotes, coordinates and implements the studies in protection, management and enhancement of the environmental resources. The Cutgana organizes workshops and conferences on various environmental themes, available not only for students but also for technicians of public and private companies. Furthermore, the Cutgana intends to develop and to spread an environmental awareness, information, education and participation in the modern society.

The Cutgana manages seven Nature Reserves of the Sicilian Region and a Marine Protected Area of the Ministry of the Environment, where innovative management models are experimented and new forms of responsible ecotourism are promoted.

Because of the known heterogeneity of the Sicilian territory, all the Nature Reserves lie also in variegated geological contexts. Therefore, in order to improve the educational aspects about the geological features of the Nature Reserves, new didactic strategies in the museum areas are recently proposed and implemented. Through some museum panels, the main geological aspects of some Nature Reserves have been described and represented. In particular, for each museum area at least two museum panels are developed. In the first panel, the regional geodynamic reconstruction and the general stratigraphic-structural evolution are described. In the second panel the representation and the explanation of peculiar geological features (stratigraphic, structural, geomorphologic or volcanological) of the specific Nature Reserve are discussed. Finally, particular attention was also focused on the terminology adopted, taking into account the variability of users of the museums (students, tourists or professionals). In fact, also through these strategies, the Cutgana wants to disseminate a greater knowledge of the Sicilian territory and to improve the environmental awareness necessary to become well-informed and responsible citizens.

# Earth Sciences and STEM initiatives: the Geology Project in the framework of "Piano Lauree Scientifiche"

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Keywords: Piano Lauree Scientifiche, STEM initiatives.

The "Piano Lauree Scientifiche" is an initiative of the Minister of Education aimed to sustain Science, Technology and Maths studies. It is active since 2005, but only in 2015 Geology courses have been included in the grant system. The "Piano" is structured in seven national disciplinary partnerships, including all the italian Universities where a BSc course is listed in their undergraduate prospectus. Then, the 29 Universities involved in the Geology Project share general and specific objectives for vocational guidance of incoming students, training of secondary school teachers, and initiatives in order to reduce the drop-out rate. The description of these objectives and the results obtained in the last three years are presented and it can stimulate the discussion in order to improve the project during the next years, when new specific tasks will be added: gender-related issues, improvement of mentoring and accompaniment initiatives, refresher training for school teachers.

# How introduce cultural heritage in science lessons: the approach of Italian developer teachers in Europeana DSI-3 project

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Keywords: European Year of Cultural Heritage, cultural heritage, teaching activity.

2018 has been designated the European Year of Cultural Heritage (EYCH) and is aimed at encouraging sharing and appreciation of Europe's cultural heritage resources; hence, a series of initiatives and events will take place across Europe aimed at emphasizing the value of cultural heritage. Some of these will be carried out targeting specifically the audience of teachers, in order to promote the inclusion of this material in lessons and activities. This is possible even because technology offer easier and better access to digitized artifacts (Ott, M., & Pozzi, F. (2008). Europeana project (https://www.europeana.eu), is the Europe's digital cultural heritage platform which aims at make cultural heritage available online for leisure, work and educational purpose. Since October 2018, the Europeana DSI-3 project involved 18 teachers around Europe to design teaching material based on cultural heritage and using digitized material from Europeana collection. The material designed during this project is available online and contributed to create a massive on line course (MOOC) on European Schoolnet Academy (http://www.europeanschoolnetacademy.eu/web/europeana-in-your-classroombuilding-21st-century-competences-with-digital-cultural-heritage). In this contribution we would present our learning scenarios that used cultural heritage material as starting point for Natural Science and Geography lessons. These activities are suitable for students of different grade (from primary to high school) and focused on topics like: geomorphology, rocks classification, evolutioncoevolution. The purpose of this work is to show an example of Science Technology Engineering Art and Mathematics (STEAM) lessons, to help Italian Science teachers in using cultural heritage materials to design Science lessons or use this digitized material during their teaching activity.

Ott, M., & Pozzi, F. (2008): ICT and cultural heritage education: Which added value?. In World Summit on Knowledge Society (pp. 131-138). Springer, Berlin, Heidelberg.

# MALIA: a project to raise awareness on Marine Litter in the Atlantic and Mediterranean Area

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Keywords: Marine litter, Ocean Conservancy, beach clean up.

Marine litter is a global problem with long term negative impacts on marine and terrestrial ecosystems and on human health. Some industries are beginning to look at the risks arising from marine litter and quantify its cost (Newman S. et al., 2015), while, for other types of activities, research is needed to determine impacts on ecosystems. Due to its global relevance it is important that topics on marine litter start to be included in educational programs to raise awareness of students. Hartley et al. (2018) highlighted that working with educators and school students is important to facilitate public understanding of complex environmental issues and to make society part of the solutions. For this reason, we are running an Erasmus+ project aimed to include marine conservation practices and marine litter educational guidelines in the national school curriculum from 4 EU countries (Portugal, Cyprus, Italy and Spain). We will prepare educational material to improve students and teachers awareness on marine litter; this will reinforce teacher role and professional development while providing an opportunity to design open educational resources. Four one-week students exchange activities are planned, one in each participating country, during which schools and associations will be involved in beach cleanup activities and they will invite local communities to join in and participate actively. During the beach cleanups, an Ocean Conservancy protocol, established in Spain with the participation of AAE, will be used to collect information on marine litter. This new protocol will be translated into the several EU languages and shared to promote beach clean up activities around Europe. Here we will present the early results of the project, including those from the first students exchange activities.

Newman, S., Watkins, E., Farmer, A., ten Brink, P., & Schweitzer, J. P. (2015): The economics of marine litter. In Marine anthropogenic litter (pp. 367-394). Springer, Cham. Hartley, B. L., Pahl, S., Holland, M., Alampei, I., Veiga, J. M., & Thompson, R. C. (2018): Turning the tide on trash: Empowering European educators and school students to tackle marine litter. Marine Policy.

### The virtuous integration of research and educational projects: examples from the Piemonte region

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Keywords: Geoheritage, Piedmont, secondary education.

In the frame of the last Piano Nazionale Lauree Scientifiche (PNLS; Italian national plan for enhancing scientific degrees), the geological community has been involved in a formal effort to bring science and research to the young generations, and to help them out in achieving in-depth knowledge and lifelong success in the STEM sciences. The short space that Earth Sciences have in the national school curricula and the poor literacy of science teachers in this subject makes this new involvement very promising.

The project has been coordinated at the national scale by the University of Firenze, but local unit in other national universities were able to personalize their activities in agreement with personal skills of the people involved and of the peculiar geological setting at the regional scale.

At the University of Torino, the Department of Earth Sciences promoted the conservation and dissemination of geological heritage through a three-year long project, PROGEO-Piemonte (PROactive management of GEOlogical heritage in the PIEMONTE region: innovative methods and functional guidelines for promoting geodiversity knowledge and supporting geoconservation activities), jointly funded by Compagnia di San Paolo and Torino University. The project developed new basic research on nine geographical areas showing peculiar geological settings, from Alpine metamorphism to glacial landscape. For each area, one or more geological tours were proposed for enhancing interest in the geoheritage of the region. These are hosted on the www.progeopiemonte.it website and on two free mobile apps: PROGEO-Piemonte, containing the geological tours, and TourInStones, devoted to the ornamental stones used in the historical buildings of the city of Torino. During the first three years of the PNLS project, several laboratory and field activities were offered to secondary school students and teachers. Some of them were hold at the GeoDidaLab, the environmental education and research laboratory of the Department of Earth Sciences. Among the topics: geodynamics ("La geodinamica in una scatola"), volcanology ("Colate di... cera!"), the origin and classification of rocks ("Il ciclo delle rocce"), the geological evolution of the southern and the northern Piemonte region. Within these last two activities, research scientists and wildlife guides tested the geological tours offered by PROGEO-Piemonte along the Tanaro valley and in the Sesia Val Grande UNESCO Geopark. The most recent achievements of the research on the topics of the Messinian Salinity Crisis and of the Sesia supervolcano were used to attract the interest of the students and teachers, combined with an inquiry-based approach, cooperative learning educational activities and the use of multimedia tools. These experiences turned out to be a live demonstration that basic research is not only interesting, but also that it permeates our daily life.

## ECORD School of Rock 2018

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Keywords: Science Education Initiative, Research Experience for Teacher (RET), Laboratory training.

"School of Rock" is an educational workshop during which teachers become familiar with the International Ocean Discovery Program (IODP), scientific drilling and Earth Sciences through the interactions with IODP scientists and former Education/Outreach Officers. This initiative was created in 2005 by the IODP US Implementing Organization (IODP-USIO) as an expedition designed for Earth and Science teachers onboard the "*JOIDES Resolution*" during a transit of the drillship. Since 2014, ECORD teachers who sailed onboard the "*JOIDES Resolution*" as Education/Outreach Officers take initiative to organize an educational workshop in their home country to share their at-sea experience and to teach their colleagues on how to bring IODP science into the classroom.

Italy has acquired the right to host the school thanks to the participation of Alessia Cicconi (IODP Expedition 367, February-April 2017) as Education/Outreach Officer. "ECORD School of Rock 2018" is held in Pavia at the Department of Earth and Environmental Sciences of the University of Pavia.

The Italian school is focused on "Paleoclimatic studies through deep sea sediments" and addressed to a group of about 20 Biology and Earth science teachers from Italian secondary schools. The school includes scientific lectures and practical hands-on activities conducted by the participants on IODP cores. This immersive experience provides Italian science teachers with an opportunity to work side-by-side with IODP scientists, using current state-of-the-art approaches to solve scientific problems of global interest, and gaining first-hand knowledge of the results of science expeditions. Invited speakers are scientists who had taken part in IODP expeditions and/or have strong expertise in climate change. They give lectures about: Timing of climate change (Patrizia Ferretti, Italy); Paleoclimate modelling (Florence Colleoni, Italy); Climate change impacts and adaptation (Sergio Castellari, Denmark).

During the practical activities, scientists and education officer lead laboratory sessions to groups of teachers on how to find and work with IODP data and test practical hands-on activities they could continue in the classrooms. The school provides discussions on how to keep in touch and share IODP resources with students.

#### Seeing the invisible. The magical world of fluorescent minerals

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Keywords: Fluorescence, Luminescence, Mineralogy.

Luminescence is the ability of a matter to emit electromagnetic radiation in the visible light range (~380-770 nm as wavelength) as result of temperature increase (thermoluminescence), mechanical stress (triboluminescence), biological reactions (bioluminescence), excitation by means of electron flux (e.g., in a cathode ray tube) or energetic electromagnetic radiations (fluorescence). The emission of visible light lasting few seconds to several minutes after the end of the perturbation of the quiet state is defined phosphorescence, while the persistence of a colour different from the pre-exposition, after the perturbation is defined as tenebrescence.

Fluorescence colour is used as diagnostic tool to identify a small amount of minerals (no more than a couple of hundreds over a total of >5300 mineral species) and the typical excitation tool is represented by UVA, UVB and UVC lights. UVA (Ultra-violet type A) lights are characterized by a peak of wavelength close to 365 nm, and UVC peak around 254 nm.

With simple experiments showing the effects of illuminating normal minerals or rocks (and specific arthropods or chicken egg shells) with UV lights it is possible to describe the electromagnetic spectrum, including x- and gamma-rays, visible light and radio waves, the origin of the colours, the adaptability of the human eyes to the environment, the origin of the solar energy, the principles of the atomic structure and quantum physics including the photoelectric effect. The outreach capacity of these simple concepts is enormous and should be used much more at all the levels of scientific careers. The use of cheap UVA lights or more expensive UVC lights has an incredible impact in activating curiosity to learn the principles of electromagnetic radiation and the origin of the colours. This is possible with immediate and fully repeatable visible effects. The cost of fluorescent minerals is much lower than typical aestetic minerals shown in museum or private collections, excluding extremely rare, and hence expensive, variants. UV shows can be done using portable equipment and can be reduced to a very small case. The only precaution is to use safety gloves and glasses to prevent burning with UV light. A powerful SW light can burn eyes in less than one minute. A couple of minutes will burn skin.

Concepts concerning the atomic structure, the quantum levels, electron orbitals, the relation between energy and wavelength, the photons, the electromagnetic spectrum and even the basic concepts of the origin of x- and gamma-rays can be introduced using simple tools like UV light sources and common minerals. When exposed to fluorescent minerals for the first time, a certain amount of people are blown away by it and go on to develop it as a hobby. This approach can foster a lifelong continued interest in science.

## Progetti ASL come esempio di sinergia tra scuola e università: la proposta del Liceo Boggio Lera di Catania sulle collezioni paleontologiche del Dipartimento BiGeA

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Keywords: Alternanza Scuola Lavoro, formazione, collezioni paleontologiche.

La proposta progettuale di Alternanza Scuola Lavoro che viene presentata prevede la creazione di un Percorso Virtuale Interattivo attraverso le Collezioni Paleontologiche del Dipartimento di Scienze Biologiche, Geologiche e Ambientali dell'Università di Catania. I destinatari, 20 studenti dei corsi scientifici del terzo anno di corso del Liceo Boggio Lera di Catania, acquisiranno competenze lavorative e formative in seguito alle seguenti attività che andranno a svolgere, per le ore che saranno necessarie nel triennio 2018-2020: - Lavoro e cooperazione di gruppo; - Apprendimento delle modalità di creazione di siti web interattivi professionali; - Arricchimento di tali competenze, e quindi approfondimento dei linguaggi specifici (html, css, java, ecc.) per la creazione di siti professionali, utili, accattivanti, facilmente navigabili, perfettamente e semplicemente interattivi: - Acquisizione delle conoscenze specifiche paleontologiche e museali quali la classificazione e riconoscimento delle specie, i processi di fossilizzazione, la conservazione dei reperti fossili e la loro esposizione. Gli obiettivi che si intendono perseguire sono i seguenti: - riconoscimento e studio dei fossili presenti nelle collezioni paleontologiche del Dipartimento; - Documentazione fotografica e video di singoli reperti o vetrine espositive e trasferimento in file di immagini (bidimensionali, tridimensionali, effetti in 3D di rotazione poliassiale); - Riorganizzazione della pagina web sulle collezioni paleontologiche del Museo di Scienze della Terra preesistente in rete attraverso più moderni strutture e sistemi di lettura; - Trasferimento dei dati (sotto forma di differenti schede tematiche) all'interno della nuova struttura interattiva; - Controllo tecnico-scientifico da parte dei docenti universitari (tutor aziendali); - Finalizzazione e successiva pubblicazione sul sito UniCT (nel caso l'Istituzione, dopo i controlli di cui al punto precedente, dia le necessarie e debite autorizzazioni in merito) per una libera e pubblica fruizione delle collezioni. Il progetto di Alternanza Scuola Lavoro qui presentato segue un precedente progetto-pilota sempre di ambito paleontologico, svoltosi nelle stesse sale espositive del Dipartimento, che ha rappresentato un importante percorso formativo. Dopo queste positive trascorse esperienze, il progetto esposto vuole rappresentare quanto di meglio si possa ottenere in termini di prodotto formativo e di acquisizione di capacità e abilità multidisciplinari da parte degli studenti di Scuole Secondarie a vocazione scientifica.

## **Remote Educational Gaming for Geosciences**

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Keywords: Geoscience Education, Game Based Learning, Remote Digital Game.

This research is based on our idea to develop a software platform for user-created role-playing adventures. A key point in favour of this type of technology is that it can be used without any programming knowledge, thus greatly amplifying the number of potential users. We then developed a computer role-playing game (CCRPG): GeoQuest. It creates an innovative learning environment, which gets the full involvement of the players, in cooperative learning and in interactive mode. We have taken into consideration the specific needs of teachers, as we believe it is essential for them to be able to work in satisfactory conditions, in order to maximize the effectiveness of the teaching action. We focused mainly on attract the students to learning Geosciences by using an interdisciplinary way, obtaining more than satisfactory results than those obtained with the traditional teaching. The project attracted the interest of Science on Stage Europe, which sponsored a Joint Project between Italy and Iceland: Icelandic students played GeoQuest Vesuvius, an adventure trail focusing on Earth Sciences, history, mythology and literature linked to the Vesuvian area in Campania. The students, assisted by their teachers, then collected the materials to create an adventure about the geology of Iceland, set-up in the traditional medieval Icelandic sagas. This adventure was played by Neapolitan students, in English, with excellent results in terms of involvement and learning. At the end of May 2018 the students of a Neapolitan high school will play the GeoQuest digital didactic game together with the Icelandic pupils: the adventure was created entirely by the students and is focused on astronomy and myth. A middle school in the Marche region will participate too, whose pupils wrote an adventure based in the Middle Age: the students also created indepth materials, digitized them and added them to the adventure pathway. Each school has therefore created a path designed and written entirely by the students, who created the subject, the storytelling, the script, the illustrative materials of various kinds, the music etc. Each of these "adventures" will be shared with students from other schools, other cities, other countries, without moving from their desk: they can challenge each other by playing the same game, connected via web!

Strengths:.

- 1. The path of the game is created by the children themselves, so the teaching value is much greater.
- 2. The groups of different countries interact remotely, know different realities, collaborate.
- 3. The use of smartphones and web gaming is an unsurpassable attraction.
- 4. The experience is easily reproducible anywhere and at any time. Experience outcomes:.
- 1. Sharing the experience of having created a game available on the platform to be played by other students.

#### Esecuzione di una traversa sismica nei locali della scuola ed elaborazione dei dati ottenuti

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Keywords: didattica delle geoscienze, indagine geofisica,QR-code.

Nel corrente A.S., il Dipartimento di Scienze dell'I.T.E. "G. Russo" di Paternò, con la collaborazione di un Geologo Libero Professionista, ha organizzato, con l'approvazione del D.S., un'indagine geofisica mediante MASW e tecnica dei rapporti spettrali o HVSR all'interno dell'area verde della scuola. I dati acquisiti sono stati, subito dopo, elaborati in Aula Magna alla presenza degli alunni che ne hanno potuto trarre le conclusioni. L'esperienza, rivolta agli alunni delle classi prime sotto forma di Potenziamento delle Scienze della Terra, ha avuto notevole successo e sarà, in futuro, riproposta e perfezionata ulteriormente, anche perché sono stati essi stessi parte attiva nella generazione di onde sismiche artificiali. I risultati emersi dall'indagine sono stati i seguenti: il terreno sul quale è stata costruita la scuola è un terreno di categoria B avendo le onde S una velocità media di 405 m/s, terreno assimilabile a depositi di terreni a grana grossa mediamente addensati o terreni a grana fine mediamente consistenti, con spessori superiori a 30 m, caratterizzati da un graduale miglioramento delle proprietà meccaniche con la profondità e da valori di Vs30 compresi tra 360 m/s e 800 m/s (Categorie del sottosuolo nelle NTC 2008).

Ciò è stato fatto, oltre che per ragioni didattiche (conoscenza e studio delle onde sismiche e strumenti per la loro rilevazione), anche per contribuire, come scuola, alla formazione del Cittadino di domani, consapevole di saper e poter affrontare temi quali: costruire in aree sismiche, conoscere le caratteristiche dei terreni sui quali costruire, ecc. Durante l'esperienza e l'elaborazione dei dati è stato girato un video dal quale è stato creato un QR-code che sarà inserito all'interno della nuova edizione del testo Book in Progress di Scienze della Terra in uso nella nostra scuola.

Inutile dire che l'argomento è collegato con molti temi di natura geologica: dalle placche tettoniche ai vulcani e ciò ha dato la possibilità di trattare tutti questi argomenti collegandoli tra di loro. Pertanto si propone, per il corso del 14 settembre, di mostrare: le modalità con le quali è stata fatta l'esperienza; i risultati.

E l'elaborazione dei dati; commentare le ricadute didattiche sugli alunni partendo dal video girato e completando con le tabelle dei risultati ottenuti. Si ritiene molto importante, come scuola, approfondire la didattica delle Geoscienze per far acquisire agli alunni una consapevolezza tale da renderli cittadini informati e responsabili su temi molto attuali quali: il rischio sismico ed idrogeologico, inquinamento, le fonti energetiche rinnovabili, ecc.

#### **Risk Detective: serious games for risk education**

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Keywords: Education, risks, geohazards.

Education on risks posed by geo-hazards is a major challenge that needs to be addressed with a bottom-up approach: starting at school in order to foster a new society, in which awareness and adaptation will promote in the long run sustainability. Risk Detective is a serious game for elementary schools that is intended to trigger students interests on hazards and risks in their surrounding environment, foster a proactive attitude towards safe behaviours and raise capacity to cope with the emergency phase of a disaster. Seismic and hydrologic hazards are the subject of the current version of Risk Detective that was implemented within the MaTer2.0 project co-financed by the Italian Ministry of Education and Research (MIUR) within the 2015 call for science dissemination; the remaining geo-hazards may be included in an upgraded version. The game has a multidisciplinary approach based on learning by competences. Disciplines involved include Language, History, Arts and STEM (Science, Technology, Engineering and Mathematics). Students are engaged with a story that resembles a real-life situation in the village of "Picchio Roso" where the lack of preventative measures towards risk mitigation turned a natural hazard into a damaging event. Students are main actors of the story, but the action starts and ends in the house of the Major. Risk management is framed as a community issue. Because risky situations have an unpredictable component that we all need to be aware of dice launches were included in the game. They will depict possible evolutions of the emergency that needs to have different solutions. The Students are required to spot hazards and vulnerability to assess risks and have a final judgement on actions that need or had to be undertaken.

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#### Challenging young scientists with Science Communication

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Keywords: Science communication, Geo-Science at school.

The engagement of society into science strongly depends on researchers' ability and efficacies in communicate their findings. The way scientists communicate, within and outside their peers' community, can even rule the success of their achievements and/or research proposals. Moreover school represents a crucial environment where to communicate science to raise interests in students, disseminate up-to-date knowledge and prompt proactive attitude towards natural hazards. Traditional scientific training, typically does not prepare scientists and engineers to be effective communicators outside of academia.

Keeping this in mind we designed a Science Communication School -a one week short-course- having as specific target young scientists that nowadays acknowledge the importance of building skills to disseminate their science to a broad range of audience. The school is intended to provide skills on how to effectively convey research results to a public of both experts and laypeople.

The lecturers do not just present an overview of science communication from a theoretical point of view, but offer practical activities on abstract/paper writing and poster editing, on proposal and report drafting, and on how to improve communication to policymakers, general public and schools even within critical contexts.

Communication to schools takes up specific session of the training and it is focussed on geo-science, acknowledging the gap in teaching such topic at school. Students are given lectures focussing on why, what and how to communicate geo-science at schools. They are provided with hints on the language, the choice of appropriate topics and the most capturing approach always keeping in mind that the age of students is one of the most important points in profiling the audience. A laboratory that gave the podium to the communication school students to practice their abilities followed the lecture. The laboratory was filmed and commented by the lecturer.

The Science Communication School, organized in Castiglione del Lago (Italy), is now at its third edition and got students from more than 20 countries spread all over the world. Here we present activities performed by the students during these three years.

#### Earthquakes, Non-Structural Elements and games - Practical solutions to reduce risk

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Keywords: risk education, science communication, Non-Structural Elements.

KnowRISK (Know your city, Reduce selSmic risK through non-structural elements) is a project co-financed by the European Commission's Humanitarian Aid and Civil Protection under the Prevention and Preparedness call 2015, that focused on communicating preventative solutions to mitigate damage caused on Non-Structural Elements (NSE, the non loading part of buildings) during earthquakes.

Although responsible for a large part of the damage occurring during moderate magnitude earthquakes, which are very frequent, prevention on such elements is often underestimated.

Among the several actions implemented by KnowRISK, a Practical Guide (PG) and a Short Students Guide (SSG) are tools intended to support communities. Four steps are coded in the Guides to assist people into a process of increasing safety, efforts and eventually cost: Move, referring to actions that just require rearranging furniture; Protect, referring to valuable fragile or expensive object; Secure, referring to large and heavy items that pose serious danger when loose; Retrofit, referring to those actions that are more intrusive and need an expert intervention. The Guide provides indication to implement, where possible, DoItYourself actions.

The guides were then turned into games to foster dialogue and interaction of the public with the experts. Here we present two games that are mostly targeted to students, but can be used to engage general public in discussing easy to be implemented solutions to reduce risks. "Do it right: be safer!" is a board game with 36 cards that depict solutions suggested in the PG, 4 avatars characters (a seismologist, an engineer, a civil protection officer, a fireman) and 4 cards with icons relative to the cost and the expertise needed to implement the solutions. These are grouped according to the Move-Protect-Secure-Retrofit concept and have to be placed on the appropriate board where they belong on the PG. In order to raise the challenge of the game and trigger discussions with the students, cards presenting wrong solutions are also added. In order to be used in an international framework, the whole game has no scripts.

"Find the difference: with and without solutions" is the board game based on the SSG. A students' bedroom and a schoolroom with and without solutions to reduce damage to NSE are compared: players are asked to spot and discuss the differences.

The games' prototype were tested during the KnowRISK final conference and successfully used during the 2018 edition of ScienzAperta in Milan.

## New methodologies and technologies in Earth Sciences education: opportunities and criticisms for future teachers

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Keywords: Geoscience education, didactical approaches.

The recent Italian regulation of the school teachers' recruitment implies a great involvement of universities for what concern students, graduated, trainees and temporary employees. A common path is represented by the acquiring of skills in anthropo-psico-pedagogic disciplines and on methodologies and technologies specific for education, according with the most recent law. Moreover, specific requisites are necessary for different subjects classification. Many Italian universities have organized specific courses in order to allow people interested to work as teachers to obtain the required skills as certified exams. In the present work, the aims and contents of the course *Earth Sciences for education* proposed at University of Milan are at first presented. Particular attention has been paid to educational projects carried out by researchers in collaboration with different teachers and secondary schools, evidencing the key role of laboratory activities as well as fieldwork (Bollati et al., 2018; Pelfini et al., 2016; Sturani et al., 2018 in press). Moreover, the relationship between Earth Sciences and Society as well as between Geosciences and Cultural Heritage, has been highlighted, always in the frame of educational strategies. Methodologies and technologies have represented a thread for different topics. Then, the results of an analysis both referred to attendees and to opportunities and criticism evidenced by anonymous questionnaires and by exam results are discussed. The main points are referred respectively to: i) composition of participants, qualification, present positions and liking ii) results related to specific Geoscience topics, analyzed from an educational point of view and related to didactical contexts.

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## Piovono idee! diventa progetto continuità

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Keywords: scuole primarie e secondarie, laboratori, giochi scientifici.

romuovere la cultura tecnico-scientifica nelle scuole primarie e secondarie di primo grado, anche attraverso l'utilizzo di laboratori e giochi scientifici fatti da materiali poveri, è stata la scelta per il progetto didattico di continuità dell'istituto comprensivo Don Milani (ex ISA1) di La Spezia per l'a.s. 2017/2018. I fruitori sono stati coinvolti in iniziative capaci di favorire la comunicazione con il mondo della ricerca per far crescere una diffusa consapevolezza sull'importanza della scienza per la vita quotidiana e per lo sviluppo sostenibile di una società dove è sempre più importante la conoscenza dell'ambiente che ci circonda e dei meccanismi che lo regolano. L'esplorazione delle Geoscienze diventa il mezzo per comprendere quelle dinamiche che conducono alla presenza dei fenomeni naturali che purtroppo spesso l'uomo sottovaluta e contribuisce a far diventare catastrofi. Attraverso un percorso attivo si parte dalla scoperta dei fenomeni geologici con esperimenti ed exhibit interattivi per terminare con dei giochi di gruppo e di ruolo che inducono alla riflessione sull'impatto ambientale dei propri comportamenti sulla collettività. La realizzazione di questa iniziativa espositiva alla scoperta del rischio idrogeologico ha sviluppato l'immaginazione attraverso la manipolazione e il gioco (learning by doing e learning by playing) e sensibilizzato gli alunni alle problematiche dell'ambiente per radicare un atteggiamento sostenibile e consapevole verso i pericoli legati ai fenomeni naturali per diventare cittadini responsabili (long life learning). Piovono idee! (ScienzAperta 2013) è stata realizzata dall'INGV e da ConUnGioco Onlus insieme ai ragazzi di 15 scuole primarie e secondarie di I grado dei comuni maggiormente colpiti dall'alluvione del 25 ottobre 2011 in collaborazione con la Provincia di La Spezia su finanziamento del Ministero del Lavoro e delle Politiche Sociali. La seconda edizione (Settimana del Pianeta Terra 2016) ha coinvolto gli studenti in attività di riprogettazione, duplicazione e restyling nell'ambito del progetto M@ter - Pianeta Terra Mare finanziato dal MIUR e ora viene riproposta alla S.M. "J. Piaget" con un allestimento sui temi Natura, Uomo, Rischio e Territorio illustrando il punto di vista dei ragazzi nei confronti dei fenomeni naturali e dei disastri da essi causati. Per la terza edizione sono stati realizzati eventi (open day, visite guidate su prenotazione) per la fruizione della mostra interattiva coinvolgendo tutti gli alunni delle classi quinte dei plessi delle scuole primarie dell'istituto comprensivo Don Milani. Conoscenza, consapevolezza, stili di vita, cittadinanza attiva: le attività didattiche realizzate in forma di percorso attivo di scoperta, di laboratorio didattico e di laboratorio scientifico per favorire l'operatività e allo stesso tempo il dialogo e la riflessione. Il laboratorio coinvolge gli alunni nel pensare, realizzare, valutare attività vissute in modo condiviso e partecipato con altri.

#### Geoscience knowledge at the end of high school: the tool IMES

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Keywords: geoscience, survey, high school.

In the last ten years, the Italian school system has undergone profound changes, starting from 2008 (Riforma Gelmini) and with the application of the new "National Indications" and "Guidelines" for the first and the second cycle of instruction, respectively (M.I.U.R. 2012, 2010). It is worth to note that both the "National Indications" for the first cycle of instruction and the "Guidelines" for liceal high school and professional and technical institutes are not prescriptive as regards the contents to be taught: it is possible to omit some topics or change their orders of relevance, if that is considered didactically justified. The absence of a standard curriculum in Earth sciences makes particularly difficult monitoring the geoscience learning results at the end of schooling, in terms of knowledges of the disciplinary contents.

In this new context, anyone interested in geoscience education need for a scientifically-based tool to survey the learning outcomes in the Earth Science discipline, at the end of schooling. The features of this survey tool should be: solid reference criteria, based on the scientific literature in the field; good psychometrics evaluation; easiness of administering and scoring.

The research we are performing in this field is addressed to investigate two issues:

- 1. Are the students at the end of high school able to answer basic Earth Science inquiries?
- 2. Do students have hard alternative conceptions about geosciences, at the end of their school curriculum?

The instrument we have developed to carry out this research is a screening tool for 'Individuation of Misconceptions at the End of Schooling' (IMES). The developed questionnaire addresses the existence of misconceptions in three areas of knowledge: Earth-Sun system, Deep time, Geology knowledge, chosen for their relevance in the building of well-informed and responsible future citizens.

We present the results of a psychometrics analysis applied to establish the reliability and validity of IMES. The 12-item, multiple-choice questionnaire was administered to a large number of students enrolled at the first year of University of Pisa in the academic years 2015/16 and 2016/17.

For the IMES screening the Cronbach's alpha reliability coefficient was 0.74 and can be considered to be highly reliable. Construct validity was assessed first by means of a principal component analysis and then by means of confirmatory factor analysis, confirms the presence of three underlying factors (Earth-Sun system, Deep time, Geology knowledge).

IMES exhibits good psychometric properties and can be used among the students to identify the occurrence of criticalities in geoscience learning.

## **Periodic Smartphone**

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Keywords: Gesociences, high school, Citizenship Education.

Chemistry: fascinating? How to link it to Earth Sciences in high schools? In everyday life we are so overwhelmed by Chemistry that we forget its inalienable contribution and ignore where the elements are coming from, neglecting the concept of non-renewable georesources. Chemistry is considered difficult by teenagers because of its language and themes, far away from reality. Geosciences are often left in the corners and in particular the teaching/learning of minerals and rocks is particularly boring! It is important, to find new ways to ensure that teenage students fall in love with these disciplines and acquire their fundamental concepts starting from their interests and scenarios to link teaching to everyday life. The ministerial indications for the first two years of secondary high schools refer to "observation and description of phenomena and simple reactions with reference to examples taken from everyday life".

In our project we adopt an inquiry based methodology: students pose and answer questions in different steps: Which are the chemical elements in your smartphone? How many elements can you find? Is the mobile phone like a mine for elements? Where these elements are coming from in nature? From which minerals? Advertising urges us to buy better phones, but what to do with the old ones? Different activities can be carried out in groups: groups will deal with metals, semi-metals, non-metals, lanthanides. The questions/answers open the possibility to introduce the concepts of environmental sustainability and Circular Economy, as strongly indicated by the EU.

Last phase of the activity will be focused on the geoscience issues, answering these questions: Where in the world can you find the elements present in your cell phone? Is there a connection between the geological setting and the presence of ore deposits? Which deposits are present in Italy/ in your area? A visit to a mining area and/or to an industry can complete the activity. The evaluation is carried out having the groups communicating their results to the all class with an oral presentation or a poster session.

The topic can be further extended to group/individual research on "Cell phones and wars" to be carried out with colleagues in History/Geography and Humanities, to answer the question: In your opinion, has the rush to extraction and exploitation of raw materials caused conflicts in the past? and today? This can represent a highly-interdisciplinary activity useful for Citizenship Education.

## The convergence of the disciplines for stage in high schools

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Keywords: Alternanza Scuola-Lavoro, Geosciences at school, Big History Project.

The scientific discoveries gained over the last 70 years now allow us to build a unitary history of the universe that gathers the contributions of many disciplines. These new vision assigns to the Earth Sciences a new and important role to promote the convergence of many disciplines in order to build a unified history of the universe and of man in it. An example of this new role can be found in the Alternanza Scuola-Lavoro ASL (combined experience of study and work). For the Liceo the ASL, is a challenge. It risks becoming another activity that is added to citizenship education, assessment by skills, university orientation. The teachers see this set of activities as an already inadequate subtraction of time. Interesting opportunities are created by engaging students and the whole class council in activities of contextualization of knowledge. Students, with a precise responsibility in a working group, experience some of the typical dynamics of a work situation. From the observation, guided by indicators, and from the evaluation of the products, the teachers can obtain useful indications for inserting the students in the business realities. The Big History Project in Earth's Science context can be the solution. The students, in groups, study the history of the Universe according, they will have the task of creating a product of their choice. "Avogadro Institute" of Biella has produced videos with Sony Vegas Pro. One has engaged in a History of the Universe in 8 minutes, the other has presented the geological history of Biella. This job could be preparatory to a subsequent ASL in a geopark. In the "A. Banfi" Liceo in Vimercate (MI) it was decided to let the whole class work in the realization of a single product as 30-minute documentary that obtained almost 1500 views on Youtube. An educational trip to the Geological Observatory of Coldigioco has introduced students to the complexity of the geological history of Italy and the international interest it raises. A subsequent inspection in Val d'Ossola, led by the Department of Earth Sciences of the University of Milan, provided the necessary information to relate the remote history of the valley with the recent one. The online attendance of a coding course allowed students to design and implement an application for mobile phones with App Inventor. From the set of evaluative elements such as group work observation tables, the daily report of the progress of the activities on a dedicated platform and the evaluation of the realized products, a profile of the student's skills can emerge, useful for a subsequent ASL insertion in a company real and also for orientation at the end of high school studies.

#### Indagine sull'Ocean Literacy in un campione di studenti della scuola secondaria di I grado

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Keywords: Mar Mediterraneo, Scienze del Mare, European Marine Science Educators Association

Ocean Literacy (OL), tradotto in italiano come "Conoscere il Mare", significa comprendere *che influenza ha il mare su di te e che influenza hai tu sul mare*.

Il movimento per l'OL, nato negli USA all'inizio di questo secolo, dal 2011 si è esteso all'Europa per azione dell'EMSEA - European Marine Science Educators Association. Nell'ambito di quest'associazione si è costituito il gruppo di lavoro EMSEA Med, interessato a promuovere l'OL nei paesi del Mediterraneo attraverso diverse attività, tra cui la ricerca didattica.

A tale scopo sono stati elaborati dei questionari per indagare la conoscenza del mare tra gli studenti della scuola primaria e secondaria di I grado. I questionari, realizzati seguendo le indicazioni didattiche di OL Scope and Sequence for Grades K-12 (NMEA, 2010), sono i primi in Europa a indagare l'OL in questa fascia d'età.

I questionari, tuttora in fase di revisione, sono stati utilizzati in quest'anno scolastico su campioni di studenti di scuola primaria e secondaria di I grado in Italia (Friuli Venezia Giulia e Liguria), Croazia (Zara) e Grecia (Creta e Macedonia) prima e dopo attività didattiche sul mare.

In questa sede sono presentati i dati preliminari relativi a un campione di studenti di scuola secondaria di I grado del Friuli Venezia Giulia, prima di un percorso didattico sulla fisica della navigazione. Gli studenti, 170 ragazzi/e provenienti da 10 classi (9 terze e 1 seconda) delle province di Trieste e Gorizia, vivono entro 12 chilometri dalla costa e hanno quindi esperienza diretta del mare, almeno della loro zona.

Il questionario, articolato in 16 domande "di conoscenza" a scelta multipla e 4 "di opinione" con scala Likert a 5 punti, indaga i 7 principi dell'OL. La valutazione preliminare dei questionari ha permesso di determinare che il tema più conosciuto riguarda il principio n°3 (*Il mare supporta una grande diversità di vita e di ecosistemi*), nel quale gli studenti ottengono l'80% di risposte esatte, seguito dal principio n°6 (*L'uomo e il mare sono inestricabilmente interconnessi*) e n°7 (*Il mare è ancora in gran parte inesplorato*). I temi meno conosciuti sono risultati il n°1 (*Sulla Terra esiste un unico grande oceano con diverse caratteristiche*, solo 40% di risposte esatte) e il n°2 (*Il mare e la vita marina determinano le caratteristiche della vita sulla terra*).

Nelle domande di opinione gli studenti sembrano aver coscienza dei legami tra il loro comportamento e le conseguenze sul mare, nonché dell'importanza economico-sociale del mare. Dal questionario emergono alcune misconcezioni sulla circolazione oceanica, sulla scala globale del ciclo dell'acqua, sull'origine dell'ossigeno atmosferico, nonché su fossili e tettonica. Gli studenti sembrano invece consapevoli della biodiversità degli ecosistemi marini, dell'origine della vita nel mare e dell'azione del mare sul clima.

Sarà interessante confrontare questi risultati con i dati ottenuti in altre regioni italiane e del Mediterraneo e in campioni di studenti più giovani, al fine di migliorare la prassi didattica con un approccio sistemico alle Scienze del Mare.

## Alla scoperta dell'Ocean Literacy con un percorso laboratoriale per la scuola primaria e secondaria di I grado

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Keywords: Scienze del Mare, Mar Mediterraneo, Ocean Literacy

Il mare è la caratteristica distintiva del "pianeta azzurro" e, attraverso il ciclo dell'acqua, il trasporto di energia, la produzione di ossigeno e l'assorbimento di  $CO_2$ , permette la vita come la conosciamo oggi, in un delicato equilibrio a rischio per l'azione antropica. Per questi motivi è evidente che conoscere il mare (Ocean Literacy, OL) è essenziale per capire e proteggere il pianeta in cui viviamo.

Ciò nonostante, le scienze del mare hanno un ruolo modesto nelle Indicazioni e Linee Guida del percorso scolastico del nostro paese, restando affidate all'interesse degli insegnati più sensibili e motivati. Per molti studenti, quindi, è possibile che la conoscenza del mare si limiti alla sola fruizione turistica. Come avvicinare il mare al vissuto personale dei nostri studenti, dando senso e realtà a concetti tanto ampi e complessi?

Per ovviare a questi limiti abbiamo realizzato un percorso laboratoriale da utilizzare in classe con attrezzature ridotte e a basso costo, ispirato ai 7 Principi che costituiscono il nucleo centrale dell'OL:

- 1. Sulla Terra esiste un unico grande oceano con diverse caratteristiche
- 2. Il mare e la vita marina determinano le caratteristiche della vita sulla terra
- 3. Il mare è un elemento fondamentale nel determinare il clima e le condizioni meteorologiche
- 4. Il mare ha reso la terra abitabile
- 5. Il mare supporta una grande diversità di vita e di ecosistemi
- 6. L'uomo e il mare sono inestricabilmente interconnessi
- 7. Il mare è ancora in gran parte inesplorato.

In questa sede intendiamo proporre alcune delle esperienze laboratoriali che abbiamo testato, elaborandole ex novo o traducendole/adattandole alla scuola italiana (primaria e secondaria di I grado) sui seguenti temi:

- correnti marine e circolazione oceanica
- dai fossili alle montagne
- ciclo dell'acqua e azione del mare sul clima
- acidificazione degli oceani e potere tampone dell'acqua di mare
- catene alimentari del Mare Mediterraneo
- beach-litter e microplastiche
- studio dei fondali marini (modello di sondaggio e ricostruzione topografia).

Proporremo inoltre alcuni spunti per attività di field-work sulla costa, a nostro avviso fondamentali soprattutto per le regioni che si affacciano sul Mediterraneo, ma non sempre accessibili per le classi, anch'esse con attrezzature e strumenti amatoriali accessibili a tutti.

## "Micro-zoniamoci" student project at Science High School "Laurana-Baldi" in Urbino (PU) - Italy

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Keywords: Microzonation, seismic hazard, geology.

"Micro-zoniamoci" project was born after some questions on "territorial risks" (for instance: "What it determines the safety of a building?", "Is my school safe?") by the last year students of Urbino Science High school. It offered the opportunity for students to understand how to obtain information about a site risk and the seismic vulnerability of a building. This goal has been reached by means of a careful (and not always easy) research of the existing information. Moreover, we applied geophysical investigation (Castellaro et al., 2005; Grimaz et al., 2012) directly to their own school buildings.

First of all, the project wants to promote awareness of the risks related to own territory and to spread the safety culture on schools, following the line suggested by the Italian Ministry of Education, University and Research, which annually invites every school to organize educational activities and/or opportunities for discussion with the aim of raising awareness on safety, risk prevention and sustainability issues.

As secondary aim, in a context of learning and collaborative study, the project wants to show to students work opportunities on several professional matters like Geology, Geophysics, Geotechnics, Seismic Engineering, etc. This project, with field practice, brought to knowledge of the above methodologies without claiming to reach a professional managing of the techniques and of the output data, but with the more general purpose of showing the way of thinking and operating in the interdisciplinary sectors. Moreover, students could deeply understand basic concepts such as "seismic hazard", "seismic risk", "site effect", "resonance frequency" and "double resonance", "seismic micro zonation".

At its completion the project generated original instrumental data and the related elaborations. These will be available to the school, public administrations and professionals.

Acknowledgments: Thanks to all the students that have participated to the project, to the head teacher Prof. ssa Guidi Claudia and to the school staff.

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#### Le Geoscienze nella scuola: esperienze di didattica paleontologica

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Keywords: didattica, scuola, paleontologia.

La docenza universitaria ha in questi ultimi anni dedicato molta attenzione ad attività divulgative rivolte agli studenti delle scuole superiori e alla formazione dei loro insegnanti. Ciò nell'ottica di una sempre maggiore interazione tra mondi troppo spesso distanti come quelli universitario e scolastico, e al fine di orientare le fasce studentesche che si approssimano al diploma verso Corsi di Laurea di Geoscienze. Vengono presentate alcune recenti esperienze di divulgazione didattica su tematiche geo-paleontologiche condotte da docenti dell'Ateneo catanese in diversi licei scientifici dell'hinterland catanese e di altre provincie siciliane e della lombardia. In particolare, sono stati attuati cicli di seminari, laboratori, percorsi multimediali e geoeventi su temi di rilevanza paleontologica, come le variazioni climatiche nel tempo, l'evoluzione biotica e la storia geologica del Mediterraneo. Alcune di queste iniziative hanno comportato l'organizzazione di convegni (Climaticamente 1 e Climaticamente 2), o di attività più articolate come diverse edizioni de "La Settimana della Diffusione della Cultura scientifica e Tecnologica", "La Settimana del Pianeta Terra", il Progetto "Le Ore del Mare" e il Progetto Bandiera RITMARE - La Ricerca Italiana per il Mare. Tirocini e progetti di Alternanza Scuola-Lavoro hanno visto la sperimentazione di alcuni percorsi formativi svolti sulle collezioni paleontologiche del Dipartimento. Particolarmente efficaci al riguardo, le attività che hanno reso protagonisti i ragazzi nella realizzazione in prima persona di: 1) brevi visite guidate delle collezioni paleontologiche; 2) pannelli esplicativi a supporto di esposizioni di fossili; 3) ricostruzioni di paleoambienti in 3D; 4) video/audio in lingua inglese. Inoltre, in linea con gli obiettivi del Piano Nazionale Lauree Scientifiche, sono stati recentemente realizzati dei Laboratori di Geoscienze per studenti di liceo scientifico (Progetto "Le ore della Terra") finalizzate a suscitare interesse verso il mondo delle scienze geo- paleontologiche. Le attività sono state svolte all'interno delle ore scolastiche presso i laboratori delle scuole richiedenti. Si è trattato di attività ludico-laboratoriali innovative che hanno stimolato la competizione attraverso la "costruzione" su pannelli tematici con tessere magnetiche della corretta sequenza di eventi geologici, paleontologici e/o biologici. Per gli insegnanti delle scuole coinvolte nel PNLS sono stati, infine, proposti seminari su temi di rilevanti attualità scientifica ed escursioni tematiche sul terreno, tutte attività di formazione per lo sviluppo di best practices volte al potenziamento della comunicazione scientifica nelle scuole.

## Dinamiche della crosta terrestre e rischio sismico

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Keywords: musei universitari, didattica scuola superiore, orientamento studenti.

Il percorso rientra nell'ambito del progetto finanziato dal MIUR "La rete dei Musei universitari italiani per l'orientamento permanente al metodo e alla cultura scientifica", che si prefigge di coordinare e monitorare in diverse sedi museali del territorio italiano azioni didattiche per valorizzare e promuovere approcci e tematiche scientifici. La finalità del percorso è l'orientamento degli studenti alle scelte di scuola superiore ed università. I Musei Civici di Reggio, partner del progetto, hanno attivato per l'anno scolastico 2017-18 sei differenti percorsi, con la partecipazione complessiva di 582 studenti.

Nel suddetto anno scolastico, una classe terza della scuola secondaria di 1° grado "Manzoni" di Reggio Emilia ha sperimentato un laboratorio riguardante la tettonica a zolle, svolgendo l'attività didattica "Dinamiche della crosta terrestre e rischio sismico" nella sede dei Musei Civici.

L'attività si è sviluppata con la seguente traccia:

- Evidenza della dinamicità interna del nostro pianeta sia con il confronto delle superfici lunare e marziana, ricche di crateri da impatto meteoritico ma prive di elementi fisiografici riconducibili ad attività endogene, sia con il collegamento Internet con l'USGS (servizio Geologico degli Stati Uniti), visionando gli eventi sismici del nostro pianeta in tempo reale.
- Discussione sulle caratteristiche reologiche delle rocce all'interno della Terra, con il supporto di campioni di plastilina, polistirolo e gomma e sull'influsso di pressione e temperatura sulle rocce stesse.
- Presentazione dei metodi investigativi usati per lo studio dell'interno della Terra, introducendo i tipi di onde, quelle longitudinali e quelle trasversali, e mostrando le loro differenti proprietà.
- Modellizzazione della tettonica a zolle a partire dalla deriva dei continenti e della espansione dei fondali oceanici, in particolare con l'apertura dell'Oceano Atlantico, per poi concludere con la migrazione dei vari continenti a partire dalla Pangea.
- Modellizzazione dei processi di subduzione e conseguenti fenomeni orogenetici con modelli in legno, cartone e strati di sabbia colorata.
- Evidenza sui processi di formazione di pieghe e di faglie, con relative classificazioni, e loro frequente distribuzione nei territori appenninici, come illustrato nelle carte geologiche.
- Discussione finale sugli accorgimenti da prendere in esame in termini di prevenzione sismica sugli edifici, sia pubblici che privati, e di comportamenti da tenere durante gli eventi sismici.

## WASTEBERG: un'attività didattica sul consumo consapevole delle Georisorse in prospettiva dell'Agenda EU 2030

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Nell'ottica dell'economia circolare, presente nell'Agenda EU 2030, è stata realizzata un'attività didattica per gli studenti di III media, con l'obiettivo di aumentare la consapevolezza sul concetto di rifiuto visto come risorsa e per farli riflettere sul consumo di risorse ed energia legato ai rifiuti. L'attenzione si è concentrata sugli imballaggi di vetro, plastica e alluminio. Prima di iniziare l'attività è stato somministrato un questionario con domande a risposta aperta per valutare la conoscenza del concetto di sviluppo sostenibile. Il test è stato ripetuto alla fine della sperimentazione, con l'aggiunta di un questionario di riflessione sull'attività svolta, per rilevare il gradimento e lo stato d'animo degli alunni. Gli alunni, in gruppi, sono stati prima chiamati a separare e pesare dei rifiuti portati in classe da casa. Successivamente è stato presentato il wasteberg, un contenitore realizzato con cartone rigido e diviso in due parti: la parte in alto, più piccola, rappresenta i rifiuti, mentre la parte inferiore, più grande, è vuota e viene riempita con delle gocce come simbolo di ciò che è stato consumato e/o prodotto per realizzare gli oggetti presenti nella "punta del wasteberg": georisorse, acqua, CO2, ore di lavoro, sfruttamento del lavoro, etc. È stata quindi posta la domanda Inquiry: quante risorse spreco quando getto 1Kg di rifiuti? che può sembrare una domanda trabocchetto ma spinge gli alunni a riflettere sul consumo di risorse nel corso dell'intero processo produttivo dell'oggetto. Ogni gruppo ha calcolato poi quanta CO<sub>2</sub>, scelta come uno dei tanti indicatori possibili, è stata emessa per la produzione di quel quantitativo di imballaggio e quanta ne viene evitata riciclando lo stesso. Questo calcolo viene fatto grazie ad una scheda operativa, per completare la quale gli alunni devono mettere in gioco anche competenze matematiche (proporzioni e percentuali). Poi ogni gruppo ha presentato e discusso il risultato del proprio lavoro. Alla fine la classe ha stilato l'elenco dei materiali che si possono riciclare con maggior risparmio socio-economico ed ambientale. Dall'analisi dei questionari è emerso che la maggioranza degli alunni ha gradito l'attività ed è soddisfatta del lavoro svolto. Per quanto riguarda la definizione di sviluppo sostenibile nelle sue 3 componenti fondamentali sociale, ambientale ed economica, prima dell'attività il 59% degli alunni aveva risposto correttamente e dopo il 71%. L'attività, positivamente accolta dagli studenti e dagli insegnanti che vi hanno partecipato, viene integrata poi da alcuni aspetti interdisciplinari che coinvolgono anche i docenti di storia/geografia e tecnologia, per rispondere alle domande: quali sono gli elementi chimici che formano questi materiali? Da quali minerali/rocce vengono estratti? Quali sono i maggiori paesi produttori nel mondo? Come sono stati utilizzati nel corso della storia? Che caratteristiche e usi hanno il vetro, la plastica, l'alluminio?

#### Il terremoto peer to peer

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D'accordo con due classi prime dell'ITE di Porto Sant'Elpidio, a seguito delle frequenti scosse sismiche degli ultimi anni, si è scelto di analizzare il fenomeno del terremoto. In due anni di attività i ragazzi hanno prima preparato dei questionari rivolti alle persone direttamente colpite dal sisma e a docenti esperti, visitando anche il dipartimento di geologia dell'Università di Camerino; poi hanno realizzato diversi poster tematici allo scopo di allestire una mostra visitabile dagli studenti delle altre classi dell'istituto e della vicina scuola media. In questo modo si è attivata un'esperienza del tipo "peer to peer" e ottenuto un feedback sull'attività, grazie all'analisi delle risposte a un questionario somministrato ai visitatori prima e dopo la mostra. Gli argomenti rappresentati nei poster e le domande poste ai visitatori sono: onde sismiche, sismogrammi e sismometri, faglie, situazione geologica dell'Italia centrale, scosse sismiche, teoria del rimbalzo elastico, vulcanelli di fango e come comportarsi durante un terremoto. I ragazzi hanno illustrato i poster ai visitatori della mostra, invitandoli ad effettuare anche delle semplici esperienze di tipo "hands-on". Un seminario conclusivo programmato per la data del 26 maggio 2018 sarà tenuto dal docente e da alcuni studenti alle terze classi della vicina scuola secondaria di I grado "G.Marconi" di Porto Sant'Elpidio. Nell'ambito di una ulteriore collaborazione peer to peer, sono stati effettuati dei laboratori didattici con gli alunni delle classi seconde della stessa scuola. Dall'analisi delle risposte ai sei questionari preparati si osserva che l'andamento percentuale di quelle giuste prima e dopo la visita alla mostra è in ogni caso incrementata e si è raddoppiata in almeno tre casi. Per circa il 10% degli studenti persistono però delle misconoscenze. L'esperienza peer to peer ha permesso agli alunni protagonisti l'acquisizione di alcune delle competenze chiave di cittadinanza da acquisire al termine dell'istruzione obbligatoria (DM 139), come quelle del saper comunicare, collaborare e partecipare. A conclusione dell'attività sono stati esaminati i dati dell'INGV che prendono in esame i terremoti con magnitudo superiore a 3 avvenuti dal 2006 a oggi e anche i loro ipocentri notando che gli anni 2009 (terremoto dell'Aquila) e 2016 (terremoto di Norcia), oltre al 2011 (tsunami che investì Fukushima), sono stati quelli più sismici. Allo stesso modo si è visto che gli ipocentri più frequenti sono situati a 10 km di profondità. Bibliografia Topping, K. J. (2005). Trends in peer learning. Educational psychology, 25(6), 631-645. SITOGRAFIA http://archivio. pubblica.istruzione.it/normativa/2007/allegati/all2 dm139new.pdf.

#### Italy - Geology in 3D

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The tradition of "geological models" in Italy dates back to the early decades of the XX century, when both the Royal Geological Survey and the Military Geographical Institute created 3D geological models of specific areas of the Italian peninsula, for educational purposes or museum exhibitions. This tradition has been lost over time, perhaps due to the high costs involved.

This project aims to introduce a new, 3D geological map of Italy, with the assumption that a synthesis map is always an important tool for information and education. This product represents the first attempt to reproduce the geological characteristics of the entire Italian territory on a 3D support.

The data used to create this innovative "geology in 3D model" derive mainly from the re-elaboration of the 1:1,000,000 scale Geological Map of Italy (Italian Geological Survey, 2011), from various synthetic maps (Bigi et al., 1983; Funiciello et al., 1979) and from the 1:50,000 scale geological maps produced within the framework of the CARG Project.

In developing this product, care was taken to apply cutting-edge -education and popularization strategies and tools, with the goal of enabling potential end-users to fully understand the geoscience behind the 3D model.

The chronostratigraphic legend is arranged in a "self-referential" way, thus ensuring rapid identification of rock successions and their main features.

More specifically, the following geological contents are displayed: 11 sedimentary units (glacial, fluviodeltaic and coastal environments, marine *s.l.*, integrated with a list of the most frequent lithologies), 9 magmatic units (2 plutonic and 7 effusive or sub-vulcanic, divided into continental and submarine), and 3 metamorphic units.

In the legend header 3D icons are shown, that enable visualizing the paleo-environments and/or the genetic contexts of the units. The basic criterion used to identify and distinguish the latter on paper is the age of their formation: Indeed, this is the only characteristic that was easily understood by all non-geologists. The chronological scale complies with the IUGS 2014 chronostratigraphic scale, with the age expressed in approximated millions of years (Ma).

The age data are proportional to the vertical extension of the tiles, graphically correlated to the geological time scale.

All individual units are marked with a specific color, whose fading indicates a chronological extension that is only valid locally.

The tectonic legend shows block diagrams that illustrate the three basic types of faults displayed: compressional, extensional and strike-slip, providing a graphic evidence of their meaning.

Bigi, G., Cosentino, D., Parotto, M., Sartori, R. & Scandone, P. (Eds) (1990-92): Structural Model of Italy, scale 1:500.000. CNR, Progetto Finalizzato Geodinamica, sottoprogetto Modello strutturale tridimensionale. S.EL.CA., Firenze.

Funiciello, R., Parotto, M. & Praturlon, A. (Coord.) (1981): Carta tettonica d'Italia, scala 1:1.500.000. CNR, Progetto Finalizzato Geodinamica. Grafica editoriale Cartografica, Roma.

Servizio Geologico d'Italia (2011): Carta Geologica d'Italia, scala 1:1.000.000. ISPRA., S.EL.CA., Firenze.

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