



MISCELLANEA INGV

Abstract Volume

2nd Congress of Società Geochimica
Italiana “From theoretical to applied
geochemistry”

July 1- 4, 2024 | Perugia, Italy



ISTITUTO NAZIONALE DI GEOFISICA E VULCANOLOGIA

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Keywords: Geochemistry; Environmental processes; Thermodynamics; Volcanic and seismic areas; Geothermics; Planetary science

Foreword

Dear participants,

it is with great pleasure that we welcome you to the Second Congress of the Italian Geochemical Society, which will be held in Perugia from the 1st to 4th of July, 2024.

Consistent with the title, From Theoretical to Applied Geochemistry, the Congress is organized into four broad thematic sessions, namely 1) Computational and Experimental Geochemistry, 2) Cosmochemistry and Planetary Sciences, 3) Environmental Geochemistry and 4) Geochemistry in Volcanic, Geothermal and Seismic Areas. More than 90 abstracts were submitted and various invited speakers accepted to be present for giving talks on their most recent discoveries in the different fields of Geochemistry. The program also includes four plenary sessions, during which eminent scientists will present their insights on a broad range of topics, delineating the prospective trajectory of geochemistry and its interconnections with other disciplines. The plenary lectures will be given by international members of the (bio)geochemical community such as Maria Cristina De Sanctis, Donato Giovannelli, Andrea Bravo and Tobias Fischer. Four invited speakers: Giulio Ottonello, Valentina Galluzzi, Mauro Masiol and Sergio Calabrese, will open each thematic session.

The congress will also be the occasion for the presentation of the four prizes for the best doctoral theses in geochemistry that the society awards every two years, in keeping with one of the society's commitments, which is the career promotion and advancement of young scientists. Thus, we are glad to announce that Abimbola Chris Ogunyele and Simone Paternostro shared the Galli Prize, Stefano Natali, Lisa Ricci and Giulio Bini won the Tongiorgi, Panichi and Tonani prizes, respectively.

This second congress of the Italian Geochemical Society could not have been realized without the sponsorship of the Umbria Region, Province of Perugia, the Municipality of Perugia and the University of Perugia. We also kindly acknowledge the support of the University of Florence (and Department of Earth Sciences), the Fondazione per l'Istruzione Agraria di Perugia, the CNR-National Research Council (and the Institute of Geosciences and Earth Resources, IGG).

A special thanks is to INGV and to President Prof. Carlo Doglioni who strongly supported and sponsored the event. Thanks are due to all the members of the organizing and scientific committees, to the conveners and to the volunteers who contributed to the organization of the congress. Alessandra Ariano, Monia Procesi, Lisa Ricci and Mauro Tieri are warmly thanked for editing this INGV Miscellanea, to Francesca Di Laura (Graphic Lab. INGV) for the graphic creations used in this congress and to Felicia Corsale who managed the realization of the T-shirts, bags and all other "INGV-branded" gadgets. Private companies (ThermoFischer, Encotech and Pollution Analytical Equipment) are kindly acknowledged for sponsoring the congress.

We hope you enjoy this congress and we strongly believe that the participation and discussion to the oral and poster sessions will be benefited by our young researchers.

*Orlando Vaselli
Carlo Cardellini
Francesco Frondini*

Awards

PREMIO PANICHI

Earth Degassing along the European Cenozoic Rift System (ECRIS): origin of fluids and quantification of the process

Lisa Ricci

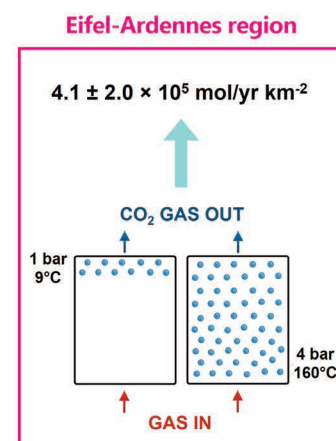
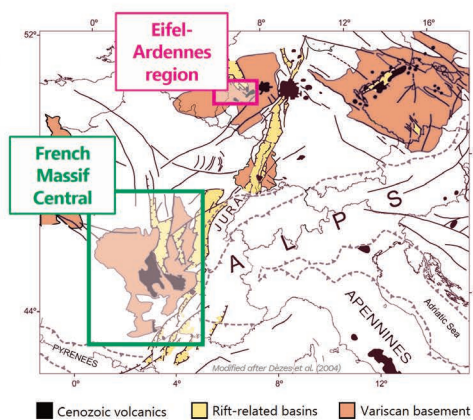
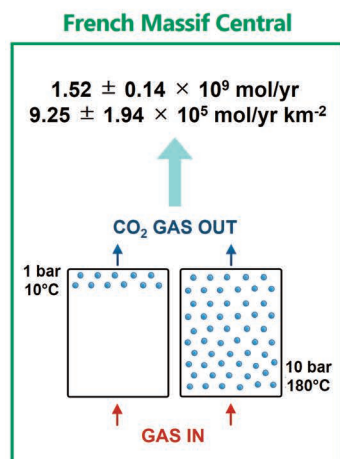
Consiglio Nazionale delle Ricerche, Istituto di Geoscienze e Georisorse, Sezione di Pisa, Pisa, Italia

The European Cenozoic Rift System (ECRIS) is a passive rift characterized by CO₂ degassing, witnessed by the presence of mineral and thermal springs, bubbling pools and mofetes. At French Massif Central and Eifel-Ardenne, two sectors of the ECRIS, water-gas-rock interaction models have led to constrain the CO₂ degassing process, which occurs in a P-T range between 10 bar, 180°C and 1 bar-10°C at French Massif Central [Ricci et al. 2024] and between 4 bar, 160°C and 1 bar, 9°C at the Eifel-Ardenne. The carbon mass and isotopic balance of groundwaters has allowed to compute the deeply-derived CO₂ emission rate of French Massif Central, corresponding to $1.52 \pm 0.14 \times 10^9$ mol yr⁻¹ and a deeply-sourced CO₂ flux of $9.25 \pm 1.94 \times 10^5$ mol yr⁻¹ km⁻² [Ricci et al. 2024]. At the Eifel-Ardenne, the estimated deep CO₂ flux is $4.1 \pm 2.0 \times 10^5$ mol yr⁻¹ km⁻². Carbon dioxide emissions are mainly driven by the regional faults occurring in the areas, suggesting a spatial variation in the magnitude of the CO₂ release within the ECRIS. The comparison of ECRIS with the East African Rift (EAR) shows that CO₂ degassing from passive rifts is about one order of magnitude lower with respect to active rifts and brings to light substantial differences in the dynamic of the degassing process characterizing passive and active rifting. The case study carried on at Bogoria lake (Eastern branch of EAR) highlights that the mantle-derived CO₂ transported by the hydrothermal system (1.39×10^9 mol yr⁻¹; $\sim 2 \times 10^6$ mol yr⁻¹ km⁻²) do not correspond to the flux to the atmosphere. This is because shallow/surface processes (i.e. precipitation of carbonates) sequester part of the deep CO₂ rising from the mantle. Both the ECRIS and the Bogoria case studies emphasise that an accurate definition of the water-gas-rock interaction processes are of primary importance to estimate the degassing process. Carbon dioxide degassing from ECRIS suggests that the CO₂ emissions from passive rifts and intra-plate extensional areas are globally significant and should be considered in the geological carbon cycle.

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Graphical Abstract



PREMIO TONANI

Interpreting the dynamics of magmatic-hydrothermal systems using the chemistry of gas emissions: the case of the Nisyros caldera (Aegean Arc, Greece)

Giulio Bini*

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Magmatic-hydrothermal systems are intricate subvolcanic environments where magmatic intrusions heat and drive fluid convection in the overlying crust. These systems involve complex physicochemical processes, such as the mixing of magmatic and meteoric fluids, fluid-rock interactions, secondary mineral precipitation, boiling and phase separation, and mixing with shallow biogenic gases. These processes can significantly alter the magmatic fluid composition before it reaches the surface, making it challenging to interpret the dynamics of these systems. This study presents new measurements of soil CO₂ emissions using the accumulation chamber method and other soil gas parameters ($\delta^{13}\text{C}_{\text{CO}_2}$, ^{222}Rn , ^{220}Rn , H₂S, temperature, and permeability), and it analyzes the chemical and isotopic compositions of vapors from 32 fumarolic vents in the southern part of the Nisyros caldera (South Aegean Volcanic Arc, Greece). The development of new techniques and comparison with previous data over the last thirty years, particularly during a seismic crisis in 1996–1997, enhances the understanding of the magmatic-hydrothermal system processes and dynamics.

CO₂ is predominantly emitted from nine diffuse degassing structures (DDS) linked to faults, hydrothermal craters, and volcanic domes. A daily release of 92 tons of CO₂ indicates the convection of 84–209 kg s⁻¹ of liquid in the shallower subvolcanic system, with a thermal energy of 134–270 Mw. After decompression and steam separation, 23 kg s⁻¹ of vapor rises and condenses near the surface, releasing 61 Mw over an area of about 2.2 km². Six months later, in April 2019, both CO₂ emissions and degassing extent in the northern area doubled. A new methodology based on carbon isotope analysis of CO₂ flux and multivariate analysis (PCA) of various parameters (CO₂ flux, $\delta^{13}\text{C}_{\text{CO}_2}$, ^{222}Rn and ^{220}Rn activities, soil temperature) allows differentiation between magmatic-hydrothermal and shallow biogenic gas emissions, revealing that variations in CO₂ emissions were due to increased biological activity rather than magmatic processes.

Nitrogen and noble gas concentration of fumarolic vents indicates a mix of magmatic, meteoric (air-saturated water, ASW), and atmospheric fluids. A reverse-mixing model technique disentangles these components and estimates their relative proportions. The magmatic volatile phase exhibits specific gas ratios and isotope signatures, with an increase in magmatic gas fractions after the 1996–1997 seismic crisis. This period also shows peaks in CO₂/CH₄ and He/CH₄ ratios and equilibrium temperature of the hydrothermal system, and increase in both fraction of vapor separated through boiling (s) and ASW. These variations occurred in response to an episode of magmatic outgassing during the seismic crisis, which led to heating and possibly deepened the vapor-liquid separation zone, causing boiling in deeper parts of the system (Figure 1). The resulting excess mass and energy were dissipated through boiling without causing hydrothermal eruptions, unlike past events in 1871–1873 and 1887. New nitrogen isotope data show a sedimentary contribution to the magma, typical of arc-volcano gases, and suggest that

the N_2 -depleted gas of the magmatic phase originated from a mature silicic reservoir after magma cooling and differentiation in the upper crust (1.5-2 kbar; Figure 1).

These findings have significant implications for understanding magmatic-hydrothermal dynamics and improving surveillance for future hydrothermal/volcanic eruptions, as enables a better quantification of volatile fluxes, mass, and thermal flows in subvolcanic systems, preventing misinterpretation of seasonal variations in soil degassing, and provides insights into magmatic gas signatures during dormant and unrest stages. This perspective on fumarole chemistry offers valuable information on magma chamber states, potentially applicable to other volcanoes worldwide for better understanding of magmatic-hydrothermal systems and eruption risks.

Graphical Abstract

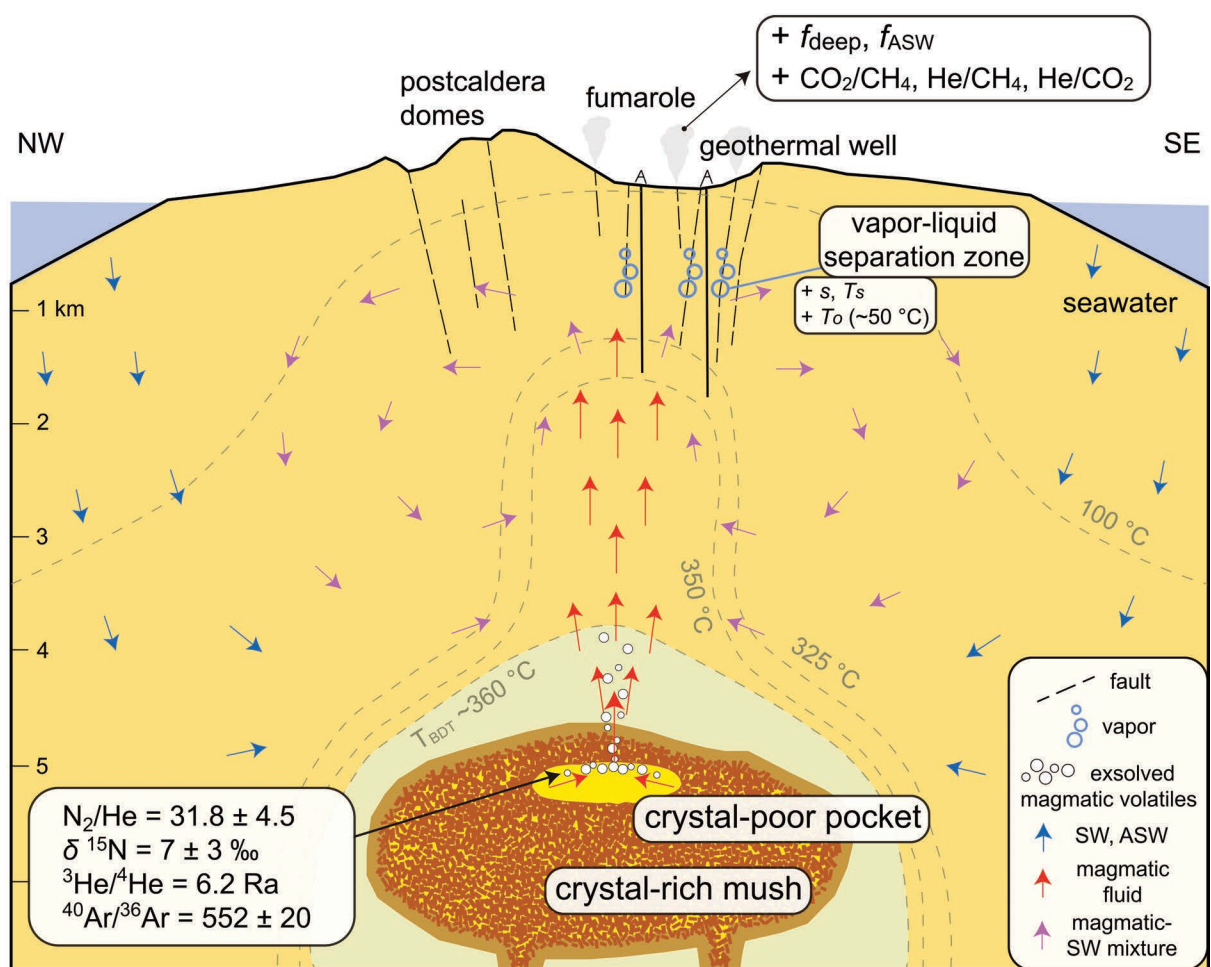


Figure 1 Conceptual model of the magmatic-hydrothermal system of the Nisyros caldera during the episode of outgassing related to the 1996–1997 seismic crisis. Evolved magmatic fluids, whose composition has been estimated through N_2 -He-Ar reverse mixing modeling, accumulate in the mature silicic reservoir and are then injected into the overlying convective hydrothermal system. This addition of magmatic fluids causes an increase in the temperature of the hydrothermal system ($\sim 50^\circ\text{C}$, reaching gas equilibrium temperature T_o of $\sim 325^\circ\text{C}$) and consequent boiling of deeper and peripheral parts, with an amount of vapor separated (s) about fifty times higher (vapor-liquid separation zone). These variations, together with the concurrent increase in fraction of magmatic fluid and ASW (f_{deep} , f_{ASW}), CO_2/CH_4 , He/CH_4 , and He/CO_2 , are recorded at the surface in fumarolic fluids.

PREMIO TONGIORGI

Isotope hydrology of precipitation and cave waters in Tuscany (western Mediterranean) in relation to moisture origin and climatic variables

Stefano Natali, PhD

Supervisor: Prof. Giovanni Zanchetta

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The stable isotope composition of oxygen and hydrogen in precipitation is a powerful tool to trace the hydrological cycle and characterize the regional atmospheric patterns. Likewise, the $\delta^{18}\text{O}$ recorded in paleoclimatic archives is a well-known proxy for reconstructing climatic variations in the recent past. O-H stable isotopes are therefore able to trace hydrological processes on different spatial and time scales. However, despite the longevity of isotope hydrology applications in the Mediterranean region, the necessity to understand the impact on the water cycle under the current warming requires new and updated views in adopting stable isotopes as hydrological tracers, both in the present and in the past.

In this PhD thesis, I investigated the influence of climatic variables and moisture origin on the isotopic precipitation composition in Tuscany (Central Italy), through the study of single meteoric events and monthly precipitation sampled at different sites. The project also aimed to evaluate the transfer mechanisms of isotope signatures from precipitation to cave drip waters, thus providing new insights into the climatic significance of $\delta^{18}\text{O}$ recorded in speleothems. The project consisted of 4 main activities: collection and processing of previously collected isotopic precipitation data into a coherent database at regional scale; systematic monitoring of monthly and event-based precipitations at different sites in two selected areas (Apuan Alps, Pianosa Island) characterized by opposite climatic regimes; Lagrangian back-trajectory analysis of precipitation; isotopic monitoring of drip waters in a karst cave in the Apuan Alps.

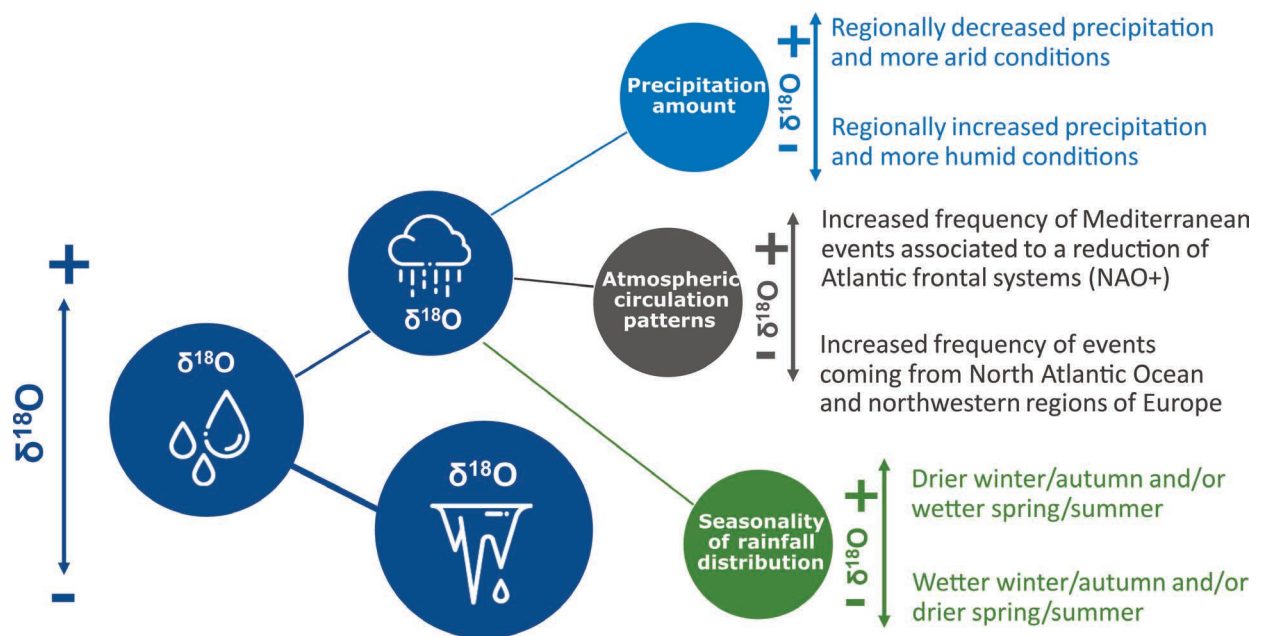
The main outcome is the quantification of the main isotopic “effects” in precipitation both at regional and more local scales. Isotope variations are rather a regionally integrated signal of several climatic and geographical variables than a proxy for either local temperature or precipitation amount. The altitude effect is the main driver of isotope spatial variability. The temperature and amount effects can explain about 50% of isotope variability in time, but whereas temperature seems to be more important in the Pianosa Island and at the regional scale, the amount effect is the major control in the Apuan Alps. These results reveal how significant differences may arise in the strength of isotopic “effects” if data are analyzed regionally or at a very local scale. Hence, main findings from global analyses can be applied in global investigations but not in local surveys, and vice versa. The source effect is the result of multiple effects, including rainout and continentality effects. Precipitations coming from more distal regions (e.g., the North Atlantic Ocean) are characterized by a long rainout distance, that amplify the effect of lower temperatures and larger precipitation by producing more depleted $\delta^{18}\text{O}$ values. On the contrary, precipitations from proximal regions (e.g., the Mediterranean basin) cover a shorter rainout distance which amplify the effect of higher temperature and lower precipitation by producing more enriched $\delta^{18}\text{O}$ values.

Spatial heterogeneity of Local Meteoric Water Lines suggests the existence of secondary

evaporation processes of raindrops during precipitation. Sub-cloud evaporation is also mostly responsible for the positive correlation between elevation and deuterium excess (d) in precipitation. d is highly sensitive to topography and local climatology, hence caution should be paid when using this parameter as a tracer of moisture sources. Conversely, d vertical gradient in precipitation on the windward side of mountain ranges could be used to constrain recharge areas of groundwater.

Finally, cave water monitoring indicate the $\delta^{18}\text{O}$ of speleothems would have the potential of recording past variations of the amount-weighted precipitation $\delta^{18}\text{O}$. Hence, the speleothem- $\delta^{18}\text{O}$ can be considered as a proxy of paleoprecipitation and interpreted as suggested in the Figure.

Graphical Abstract



Schematic of possible interpretation of $\delta^{18}\text{O}$ variations recorded in cave speleothems in the investigated area according to main findings from this PhD thesis.

PREMIO GALLI

The geodynamic evolution of the Gondwana–Laurasia boundary in Triassic times: Constraints from the tectono-magmatic cycles of the Southern Alps

Abimbola Chris Ogunyele

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The Triassic geodynamic evolution of the Gondwana–Laurasia boundary in the area now corresponding to the Southern Alps is complex and has been a subject of debate in the last five decades. The Southern Alps located at the northern margin of the Adriatic Plate was marked by the development of carbonate platforms and basins, and widespread magmatic activity during the Triassic. Detailed petrological and geochemical studies of these Triassic magmatic events have been conducted mainly in the eastern sector (e.g., Dolomites, Julian Alps, Vicentinian Alps, etc) of the region. However, many details and datasets on the Triassic magmatic events in the Southern Alps especially in the western (Ivrea-Verbano Zone, IVZ) and central (Brescian Prealps) sectors are still lacking, hence, a complete picture of the tectono-magmatic framework of the region is unavailable. This issue is further complicated by the complex paleogeography of the Adriatic Plate during and after the Variscan orogenic cycle, and the widespread hydrothermal alteration of Triassic outcrops in the region. These knowledge and data gaps were addressed in this study. The study, reported herein [and in Ogunyele 2024; Ogunyele et al. 2024a, 2024b], applied a multidisciplinary approach including detailed field observation, petrography, geochemistry, geochemical modeling, geochronology and radiogenic (Nd-Sr-Hf-Pb) isotope systematics on Triassic-Early Jurassic magmatic rocks occurring in the Southern Alps, with special focus on the westernmost (Ivrea-Verbano Zone, IVZ) and eastern (Dolomites) sectors of the region. Additional details on the Southern Alps Triassic tectono-magmatic evolution were provided by the study of orogenic mantle massifs exposed in the IVZ which could represent first-hand analogues of the mantle sources of Triassic magmatism in the area. The results of this study indicates a geochemical change of Triassic-Early Jurassic magmatic events throughout the Southern Alps from orogenic-like magmatism, typical of post-collisional settings, to anorogenic alkaline magmatism, common in intraplate to extensional settings, during the Late Triassic (Figure 1). This geochemical shift is related to a change of the mantle sources of these contrasting magmatism from a metasomatized lithospheric mantle containing significant amount of recycled continental crust components (similar to the Finero phlogopite peridotite) to variably depleted asthenospheric sources. A revised geodynamic model is proposed whereby the magmatism were triggered by the Paleotethys subduction but the recycled continental crust materials in the mantle sources of these magmatism are related to crustal materials brought down to mantle depths by the Variscan and/or older subduction events, as well as by the delamination of the roots of the Variscan chain. The recycling of continental crust materials in the mantle beneath the Southern Alps is further testified to by the enriched isotopic composition of the Finero peridotite (Figure 1) and the occurrence of the “DUPAL-like isotope anomaly” in this mantle body.

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Graphical Abstract

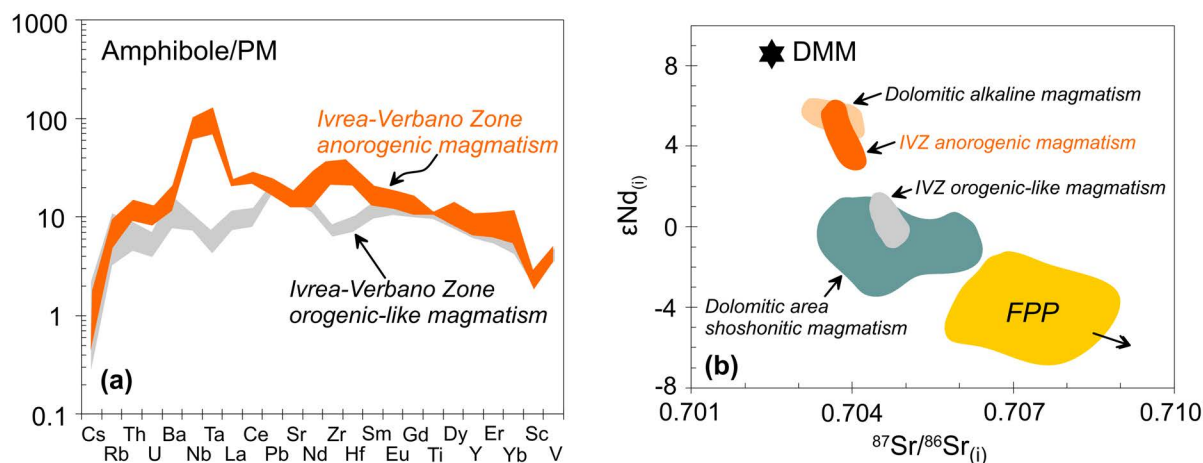


Figure 1 a) PM-normalized incompatible trace elements compositions of amphiboles from Triassic orogenic-like and anorogenic magmatic rocks from Ivrea-Verbano Zone (IVZ), western Southern Alps. b) $\epsilon\text{Nd}(i)$ and $^{87}\text{Sr}/^{86}\text{Sr}(i)$ compositions of the IVZ and Dolomitic Triassic orogenic-like and anorogenic magmatisms. The composition of the Finero Phlogopite Peridotite (FPP, 300 Ma) and Depleted MORB Mantle (DMM, 200 Ma) are also plotted. Plotted data are from this study and literature [see Ogunyele 2024].

Evaluation of the thermal potential of the Amiata Geothermal Field: Geochemical, Petrologic and Petrophysic data

Paternostro Simone

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Monte Amiata is a hybrid volcano outpoured between 305 and 231 ka during the middle-Pleistocene. Their products consist of a succession of lavas and domes, with a composition from trachyte/trachydacite to olivine-latitude. The volcano builds his edifice during a magmatic emission from an eruptive fissure aligned along the NNE-SSW direction. The eruptive activity took place in two-short lived episodes, seemingly separated from a saprolitic level characterised by a strong weather alteration. The area around the volcano underwent a regional uplift of about 2 km, extending from Monte Amiata to Radicofani volcanoes, covering an area of 35 x 50 km caused by an unspecified magma intrusion at a depth of 5-7 km.

This work employs a multidisciplinary approach encompassing the stratigraphic definition, petrographic investigations, geochemistry analyses, mineral chemistry and isotope chemistry investigations, X-ray diffraction and crystal chemistry of brown micas, microthermometry and thermobarometry experiments and calculations, melt inclusion analyses, seismic velocities and thermal conductivity properties. Results of isotopic and mineralogical investigations suggest a single extrusive eruption involved in the setting of lavas and domes. The petrogenesis of the high-silica magmas could be explained by the intrusion of sub-crustal mantle-derived HKCA/SHO magmas, which undergoes a process of R_x MFC due to the progressive injection of hot mafic magmas similar in composition to Roman-type magmas. The compositional variability observed in the groundmass glasses represents the last stage in the magmatic differentiation of high-silica rocks, and models indicate the potential presence of micro-assimilation processes of peraluminous melts/fluids release from pelitic xenoliths undergoing pyrometamorphic processes. Temperature, pressure and water content investigated by experimental and empirical approaches, reveals a shallow hypabyssal magmatic reservoir with deep mafic roots, characterised by a T-P range of 900 – 1170 °C and 0.1 – 0.9 GPa, respectively. The large amount of CO₂ indicates that mantle processes are the main players, also influencing the amount of water dissolved in magma and enrichments of carbon-rich fluids from crustal xenoliths cannot be excluded. The architecture of the magma chamber of Monte Amiata volcano can be idealised with a batholith-shape divided into two zones with different thermo-chemical features, characterised by a differentiated rock in the most marginal inner zone of the magmatic reservoir and a contact aureole in the outer zone, and mafic roots deep down. The calculated present-day temperature emitted by the heat source is about 820 °C, quantifiable by 10²⁴ calories emitted per km³, and a maximum theoretical energy production of 3277 Mw/year or 0.33 GW_{yt}.

PLENARY SESSION

Organic matter composition control the formation of methylmercury: a cross system overview

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One major challenge in contemporary environmental science is to identify factors controlling the formation of the extremely toxic methylmercury (MeHg). The formation of MeHg is biotically mediated in aquatic systems. Although it is well known that organic matter (OM) interacts very strongly with Hg, the influence of the molecular composition of OM in MeHg formation remains poorly understood. Here we show the impact of terrigenous and planktonic derived OM on Hg methylation in different aquatic ecosystems. Concretely, we studied Hg methylation in sediments of 10 lakes, 9 beaver pond and 23 river ecosystems. While the selected lakes and rivers receive inputs of both terrigenous and in situ OM, sediments collected in beaver ponds are primarily dominated by terrigenous OM with different degradation status. We used inorganic mercury isotope tracers to determine mercury methylation and pyrolysis–gas chromatography mass spectrometry and/or optical measurements (spectrometry and fluorescence) to characterize the composition OM in the sediment or at their overlying waters. The characterization of OM suggests that, in lake sediments and river waters, algal-derived compounds primarily control Hg methylation by enhancing the activity of the whole microbial community. In beaver ponds, the qualitative analysis of the dissolved organic matter water with excitation-emission-matrix fluorescence spectroscopy at the overlying indicates that, besides the role of algal derived organic matter, unprocessed terrestrial organic matter also enhances Hg methylation. We thus conclude that algal derived compounds are the main driver of Hg methylation, but in systems limited by autochthonous sources, fresh terrigenous OM play an important role on the process.

Ceres: the innermost water rich world

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Of all the solar system worlds known to possess a substantial (>10 wt %) ice fraction, none is as close to the Sun as Ceres. On the dark surface of Ceres, punctuated by small bright areas, many chemical compounds have been detected with VIR, the Italian spectrometer onboard of the NASA Dawn spacecraft. VIR has revealed that the surface of Ceres is dominated by a mixture of Mg-Phyllosilicates, ammoniated clays, Ca/Mg carbonates, and a darkening agent whose nature is still not completely defined [De Sanctis et al., 2015]. The distribution of these materials show relatively minor regional variations, interpreted as evidence for an in situ origin resulting from a global ocean [Ammannito et al., 2016]. The VIR observations also indicate the global presence of 5–15 vol% of low-solubility carbonates (e.g., calcite, magnesite, dolomite). Added to this global mineralogy, there are localized areas rich of other mineral species. Na_2CO_3 , the dominant mineral of the bright features [De Sanctis et al., 2016], implies the existence of low-eutectic brines, such as chloride solutions at depth. Indeed, fresh hydrohalite as well as sodium carbonate in hydrous forms have been detected [Carrozzo et al., 2018; De Sanctis et al., 2021], confirming the presence of salty fluids in the subsurface. Na_2CO_3 and NaHCO_3 have also been found in Enceladus's plumes [Postberg et al., 2011] and interpreted as evidence for the presence of alkaline conditions in Enceladus's ocean. The bright deposits on Ceres also include ammonium salts and chlorides, consistent with alkaline fluids. Taken together, these observations suggest that Na_2CO_3 or a possible precursor, as NaHCO_3 or its hydrates, is available in Ceres's subsurface. Moreover, clear aliphatic organics have been also observed at Ceres' surface [De Sanctis et al., 2017]. Here we will review the Dawn results in terms of Ceres formation and relevance in astrobiological context.

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The Deep Carbon Cycle: Perspectives from Volcanic Degassing

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The return of crustal carbon into the Earth's mantle is enabling outgassing of CO₂ through volcanism [Dasgupta, 2013]. The sources and fate of this recycled crustal carbon is still controversial. Subducted oceanic lithosphere carries sedimentary and crustal carbon to the trench. This C input globally is dominated by carbonates from sediments over carbonates from the altered oceanic crust (AOC) with 5×10^{12} mol C/yr ($\pm 50\%$) [Plank and Manning, 2019]. Total flux of C from arc volcanoes is about 1.1×10^{12} mol/yr [Fischer et al., 2019] and more with diffuse CO₂ [Cardellini et al., 2022]. Still, on a global scale, subducted carbonate sediment can supply the C output. The majority of $\delta^{13}\text{C}$ values of arc gases are heavier than -10% [Mason et al., 2017; Werner et al., 2019]. $\delta^{13}\text{C}$ of AOC is $0.8 \pm 0.5 \text{ ‰}$ [Alt, 2003] and subducted organic C is $\sim -20\%$ [Sano and Marty, 1995]. However, recent work on AOC shows that $\delta^{13}\text{C}$ values can be as light as -24% [Li et al., 2019]. The amount of subducted material varies depending on locality and therefore, global approaches of isotopic and flux balances obscure C recycling efficiencies [Plank and Manning, 2019]. The arcs of Colombia, Central America and Aleutians provide the complete range of volcanic gas $\delta^{13}\text{C}$ values and varying subduction inputs. In the Colombian and Central American arcs the contribution of C from the AOC is not required to supply the volcanic CO₂ output while in the Aleutians it is only 6-9% [Lopez et al., 2023]. The delivery of AOC-derived light C to the deep mantle is consistent with the C isotopes of eclogitic diamonds [Li et al., 2019]. If this is a global phenomenon, the flux of AOC C is almost equal to the C flux from MOR, 1.32×10^{12} mol/yr [Hauri et al., 2019] but quantifying the amount of C that makes diamonds [Li et al., 2019], is stored below cratons [Foley and Fischer, 2017] and removed from the mantle background is challenging. Future work is needed to arrive at consistent global C and other volatile budgets.

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Geosphere-Biosphere interactions: 10 ways biology interacts with the solid Earth

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Geosphere and Biosphere have coevolved for the past 4 billion years influencing each other evolutionary trajectory, ensuring the habitability of our planet throughout its history [Jelen et al., 2016]. While geological and biological processes have been extensively studied over the past decades, and the influence of geological processes on the biosphere has been characterized in detail. On the contrary, the influence of biological processes on geological processes has been underestimated, and beyond the well studied Great Oxidation Event, most interactions have been seen as unidirectional, with geological, abiotic processes influencing the evolutionary trajectory of life. In recent years it has become apparent that Earth's history is marked by intricate interactions between the biosphere and the solid Earth, often characterized by feedback mechanisms that significantly impact their evolution [Giovannelli, 2023]. Fundamental properties of life itself play a crucial role in these interactions, offering insights into the feedback mechanisms at the interface between the geosphere and the biosphere. For instance, metabolic processes of microorganisms can influence mineral formation and weathering processes, which in turn can alter the availability of nutrients essential for life. Life can directly or indirectly influence a number of geological processes, including the cycling of elements like carbon, nitrogen, and sulfur ultimately influencing Earth processes in unexpected and often understudied ways. Here, I will explore ten fundamental properties of life from an Earth System Science perspective and discuss how these properties influence the solid Earth. By understanding these interactions, we can gain deeper insights into the coevolution of life and Earth and better appreciate the dynamic balance that has sustained our planet's habitability through deep time.

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SESSION 1 - COMPUTATIONAL AND EXPERIMENTAL GEOCHEMISTRY

Conveners:

Devis Di Tommaso (Queen Mary University of London), Caterina Gozzi (DST, Università di Firenze), Mattia La Fortezza (DISTAV, Università di Genova)

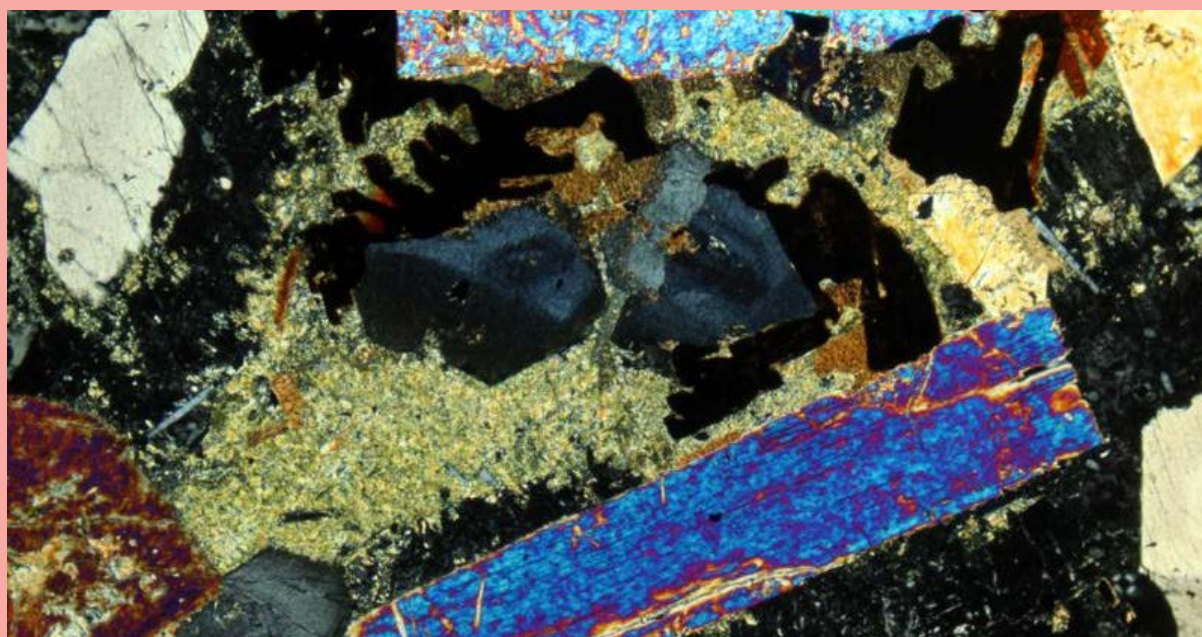


Figure caption: COMPUTATIONAL AND EXPERIMENTAL GEOCHEMISTRY da blog @AlexStreikeisen

The CMAS simplex

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The system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS) is a 3rd-order simplex of overwhelming importance in Mantle petrology. More than 100 phases nucleate in the system and more than 10 of them exhibit complete miscibility. The realm of P-T conditions of interest spans 150 GPa and 5000 K. CMAS is perhaps the most investigated system by Petrologists but, in spite of the excellent quality of experiments, the interpretation of its Schreinemaker's P,T projections is flawed by unacceptable assessments of the thermophysical-thermodynamic properties of the liquid and the solids and by redundant adoption of ad-hoc parameters, violating Occam's razor. Through the years it appeared evident to us that the thermodynamic-thermophysical properties of the nucleating solids must be validated by sound *ab-initio* procedures and that the *quasi-chemical* approaches, generally adopted to depict the mixing properties of the liquid aggregation state, though quite "*flexible*", must be replaced by polymer models exploiting the Lux-Flood basicity contrast of intervening oxides as a reactivity guide. The simplex, after simplicial mesh De-Launay fragmentation, is analyzed with convex-hull techniques and the primary-phase fields, their divariant intersections, univariant descent lines and invariant points are conveniently depicted at the light of the Gibbs free energy minimization principle.

The SCHOTTA Project: experimental, analytical and modeling studies of the seismic cycle under hydrothermal conditions

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Geophysical investigations of exposed faults suggest that earthquakes nucleate and propagate often in the presence of fluids at hydrothermal conditions ($150^{\circ}\text{C} < T < 450^{\circ}\text{C}$ and $P_f > 25 \text{ MPa}$). In fact, hydrothermal fluids can drive fault mechanics during the seismic cycle by pore pressure increase, mineral dissolution/precipitation and consequent sub-critical crack growth, sealing and healing. Unfortunately, little is known about the role of hot and pressurized fluids in rock deformation upon rupture due to technical difficulties in experiments and timescale of fluid-rock reactions which prevent direct observations.

The project SCHOTTA (*The Seismic Cycle under HydrOThermal conditions: experimenTAl, analytical and modeling studies*), funded by Unione Europea-Next Generation EU - PRIN 2022, aims to cover this gap by combining unique laboratory rock friction experiments in the presence of hot and pressurized fluids (up to supercritical water conditions) with geochemical and mineralogical analyses of fluids and rocks carried out both before and after experiments. Geochemical models, properly calibrated from analytical, petrographic and chemical data, will be employed to simulate fluid-rock interaction over time, constraining thermodynamic and kinetic datasets to extrapolate the experimental observations to natural faults. Model calibration at investigated extreme conditions is a needed challenge since the most used geochemical softwares are limited to water sub-critical conditions ($T < 300^{\circ}\text{C}$, $P_f < 8.6 \text{ MPa}$).

This innovative multidisciplinary study will allow us to identify: i) the main factors responsible for the seismic behavior of natural faults at hydrothermal conditions and ii) how the fluid-rock interaction is related to rock deformation. Finally, we will evaluate outcomes for the natural and induced seismicity developing in geothermal and volcanic settings.

GEOCH v2.0 - Retrieving a historical fluid geochemical database Bringing the Past Back to Life - Retrieving GEOCH a Historical geochemical database

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GEOCH is a relational database developed in the early 1980s and dedicated to collecting of fluid geochemical data mainly produced in the framework of volcanic surveillance on the active Italian volcanoes and during the geothermal exploration activities in central and southern Italy [Principe and Romano, 1987; 1989]. Outdated from an informatics perspective, the structure of the GEOCH database consists of a data collection of chemical analyses of water and fumarolic fluids sampled in volcanic areas, accompanied by information regarding their sampling methods and analytical treatment. The data contained in GEOCH, over 33,000 records, are sourced from: i) internal reports of the National Group for Volcanology (NGV); ii) internal reports of Joint Venture ENEL-AGIP, geothermal branch; iii) papers in national and international scientific journals; iv) papers of the last three centuries concerning analyses of geochemical fluids from Italian volcanoes. Some of these data sources are not of easy-access nowadays. Even if GEOCH represents a significant and valuable scientific resource, currently it has an outdated and inoperable informatic structure. It requires requalification and reorganization to keep this valuable data alive and permit its dissemination among the scientific community. For this purpose, the entire database and the web interface for data visualization and consultation have been redesigned. Specifically, a new conceptual data model was developed based on the original schema, and a new MySQL relational database was established. This facilitated the creation of an SQL script to extract data from the obsolete database and insert them into the tables of the new database. The imported data underwent comprehensive analysis to eliminate duplicates and incorporate additional information (e.g., bibliography). Finally, to re-enable access to the data, a web platform (HTML, jQuery, Php) was constructed for tabular data consultation utilizing the new database.

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Aqueous Phase Stability of Cu-Fe-Zn-Sn-S: A Computational Thermodynamics Perspective

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A comprehensive study of the thermodynamic stability of the structurally close Cu-Fe-Zn-Sn-S multinary sulphides, materials critical to advancing semiconductor technologies, is presented. We integrate a novel numerical extrapolation method, derived from experimental thermochemical stability constants, with PHREEQC's simulation capabilities to map the stability domains of these phases in aqueous environments. PHREEQC numerical modelling was applied to generate Pourbaix diagrams illustrating the stability fields of these sulphides under different environmental conditions.

When the scientific literature lacks the necessary thermodynamic data, one way to populate the thermochemical database could be to set up calculated values obtained by linear combination of "molecular" fragments obtainable from the known phases. This approach is very similar to the Born-Haber cycles and is based on the first principle of thermodynamics.

This analysis fills a critical knowledge gap in the aqueous stability of these phases and introduces a robust framework for predicting their environmental and technological viability. The calculated Pourbaix diagrams shed light on the relative stability and precipitation boundaries of the Cu-Fe-Zn-Sn-S multinary sulphides phases, providing invaluable insights for the development of sustainable semiconductor applications.

Thus, this research not only contributes to the theoretical understanding of multinary sulphide systems, but also lays the groundwork for their practical application in green technologies.

A mineralogical and geochemical approach for assessing the redox capacity of basaltic glass and crystals via experimental evaluation

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Worldwide, there has been an increase in greenhouse gases, particularly CO₂. To combat this problem, research and development efforts have been focused on carbon capture and storage (CCS) technology to reduce atmospheric CO₂ concentration. Among the different methods examined, mineral carbonation is a technique that involves the reaction between CO₂ and basaltic rocks. This technique stores CO₂ in the rocks by forming carbonate minerals. The approach that was used in the CarbFix project in Iceland is a good demonstration of this technique. Nevertheless, a great deal of knowledge is yet to be gained about the physical and chemical connections between water, dissolved ions, and crystal growth in complicated, multifaceted systems at the atomic and nanoscale levels. This knowledge is vital to successfully implementing carbon capture and storage in basaltic reservoirs. One approach examined in this research involves using supercritical CO₂, which is attained above the critical temperature and pressure of 30.97 °C and 73.773 bar, respectively. In these conditions, CO₂ displays the characteristics of both a liquid and a gas. This study presents the findings of experiments conducted on basaltic crystals and basaltic glasses under temperatures and pressures ranging from 100 to 200 °C and 64 to 79 bar, to investigate the reactions occurring between CO₂ (sc), water, crystals (mainly forsterite) and basaltic glass. The results showed that under these conditions, there was partial dissolution of minerals and subsequent formation of new alteration phases, as well as the precipitation of carbonates containing Ca, Mg, and Fe. Furthermore, thanks to the study of the composition of the post-reaction gases, the redox capacity of both the reaction between water-CO₂-basaltic glass and between water-CO₂-basaltic crystals will be evaluated.

Potential reuse of recycled concrete aggregates from the Umbria region after ex-situ carbonation

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Carbonation spontaneously occurs in concretes, that is, the hydration phases of cement react with CO₂ and become carbonates. Exposing Construction and Demolition Wastes (CDW) to high CO₂ concentrations is a strategy to increase the amount of captured CO₂. In this work, we study the recycling of CDW coupling a thermal reactivation process with subsequent aqueous accelerated carbonation to enhance the CO₂ capture. The used materials come from the 2016 Umbria-Marche Earthquake landfilled in Norcia (PG) by Valle Umbra Servizi. After the heat treatment, the resulting material was crushed, homogenized, and sieved at 75µm grain size. Direct aqueous carbonation was performed, and four experiments were conducted lasting 15, 30, 45 and 60 min each, with a continuous flow of CO₂ at a partial pressure of 1 bar and room temperature (RT). Preliminary results show that the first minerals to be carbonated are CaO and portlandite (CH), followed by ettringite and finally C-S-A-H, in agreement with literature data. After the first 15 min of carbonation (1) the consumption of CH and ettringite is balanced by an increase in calcite of ~20 wt.%, that remains constant in the other experiments and (2) an increase in the amorphous fraction, composed by a silica-alumina gel, compared to the samples after thermal treatment was observed, that might be related to the newly formed cement hydration phases after the reactivation procedure. Concluding, the results show that the accelerated carbonation is a non-time-and energy-consuming process, since after 15 min the CO₂ completely reacts with CaO and CH, that were formed during the heat treatment by the decomposition of C-S-A-H and takes place at ambient pressure and with a 1 bar CO₂ flow. Further studies and analyses are in progress and will be presented, particularly devoted to analysing the kinetics of such processes and optimizing the reaction times. The work was carried out under the contribution of the Fondazione Perugia: p.c. n° 21042.

Real time ammonium ion-selective electrode correction through speciation calculation in seawater

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Ion-selective electrodes (ISEs) are widely used in environmental water analysis as ideal probes for *in-situ* and *real-time* acquisition of chemical information [Crespo, 2017]. However, interference from other species is known to affect the electrochemical signature, leading to an overestimation of the target species [Cuartero, 2021]. For this reason, use of ISEs is limited to low ionic strength continental waters, approximating a Nernstian behavior. In seawater the high ionic strength and the high concentration of interfering species alter the EMF reading and make the ISE use very difficult. In this case the EMF depends on both primary and interfering species activities, which are no longer negligible, according to Nikolskii-Eisenman equation (NE). NE equation allows, through selectivity coefficients, to correct the content of the primary species taking into account one or more interferents. A general method based on a hardware-software coupling allow to calculate the NE *on-board* to correct the ISE EMF reading, is presented after lab testing using NH_4^+ ISE. This choice has been done for two reasons. Firstly, ammonium serves as an indicator of seawater quality as for the eutrophication index TRIX. Secondly, the NH_4^+ ISE is susceptible to interference from K^+ and Na^+ , two major ions present in seawater. The experiments were conducted on controlled solutions and supported by PHREEQC, which allows to work directly with species activities rather than concentrations. The method is adaptable to any ISE where the speciation of the interferent species is known, as a first step towards real-time seawater monitoring. Synthetic seawater tests, which can be easily extended to offshore applications, use the salinity (S) parameter, measured by a multi-parameter device, coupled with the Principle of Constant Proportions [Forchhammer, 1864] to estimate K^+ and Na^+ activities and remove the apparent concentration from the signal to provide a reliable estimate of NH_4^+ activity in solution.

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Isotopic composition of boron adsorbed on calcite and aragonite in seawater: an experimental and modelling study

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The boron isotopic composition of marine carbonates has been successfully used for over thirty years to reconstruct past ocean pH and corresponding level of atmospheric CO₂, providing also key insights into biomineralization processes. However, recent studies have challenged the fundamental assumptions of the B paleo-pH proxy, showing that borate ions adsorbed or incorporated by calcite structure can exhibit a significant isotope fractionation relative to the free ion in solution [Noireaux et al., 2015; Saldi et al., 2018].

To better understand the role of seawater chemistry and the mechanisms that control the boron isotopic signature of marine carbonates we studied B adsorption on calcite and aragonite surfaces as a function of pH in artificial seawater and in NaCl aqueous solution of the same ionic strength (NaCl 0.5 M). pH-dependent B adsorption on aragonite is about 4 times stronger than on calcite, in agreement with the partition coefficient data reported in the literature for the two polymorphs. Significant differences in B adsorption behavior have been observed between NaCl solutions and seawater at pH > 8.7. Such discrepancy can be explained with partial adsorption of Mg-borate complexes and with B co-precipitation with secondary brucite in seawater alkaline solutions.

B adsorption data on calcite and aragonite were modelled with the most recent version of the three-plane surface complexation model (TPM) developed for calcite cleavage surfaces [Heberling et al., 2021]. Within this theoretical framework, boron adsorption on both carbonates involves the formation of a dominant borate exchange complex, substituting for CO₃²⁻ groups at the mineral surface, and an outer-sphere complex formed by B(OH)₄⁻ adsorption onto protonated calcium sites. The following analysis and interpretation of B isotopic data suggest that B surface complexes are enriched in ¹¹B compared to aqueous borate, showing a stronger isotope fractionation on calcite than on aragonite surface.

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From Fundamental Studies of CO₂ Mineralisation to Functional Minerals

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CO₂ mineralization via aqueous carbonate formation can reuse captured CO₂ to manufacture carbon-negative materials that mitigate or even replace conventional infrastructure materials. Magnesium carbonate (MgCO₃) is of particular interest due to its importance in industrial applications but its slow growth rates under ambient conditions pose a challenge. We report the use a computational-experimental approach to resolve the nano- to mesoscopic phenomena controlling the CO₂-to-MgCO₃ conversion. The principal difficulty for the slow precipitation of MgCO₃ arises from the very strong Mg²⁺...H₂O interaction, raising barriers to Mg-dehydration. We have used atomistic simulations, complemented by spectroscopic experiments, to investigate the influence of solution additives, ranging from simple halides to more complex molecules, on the early stages of aqueous MgCO₃ formation: Mg²⁺ dehydration and pre-nucleation Mg²⁺...CO₃²⁻ pairing (**Figure 1**). Simulations of hydrated Mg²⁺, in the absence and presence of several solution additive anions, show that in pure water the metal aquo metal complex, Mg(H₂O)₆²⁺, is the only stable coordination state; yet anions may stabilise undercoordinated five-hydration configurations.

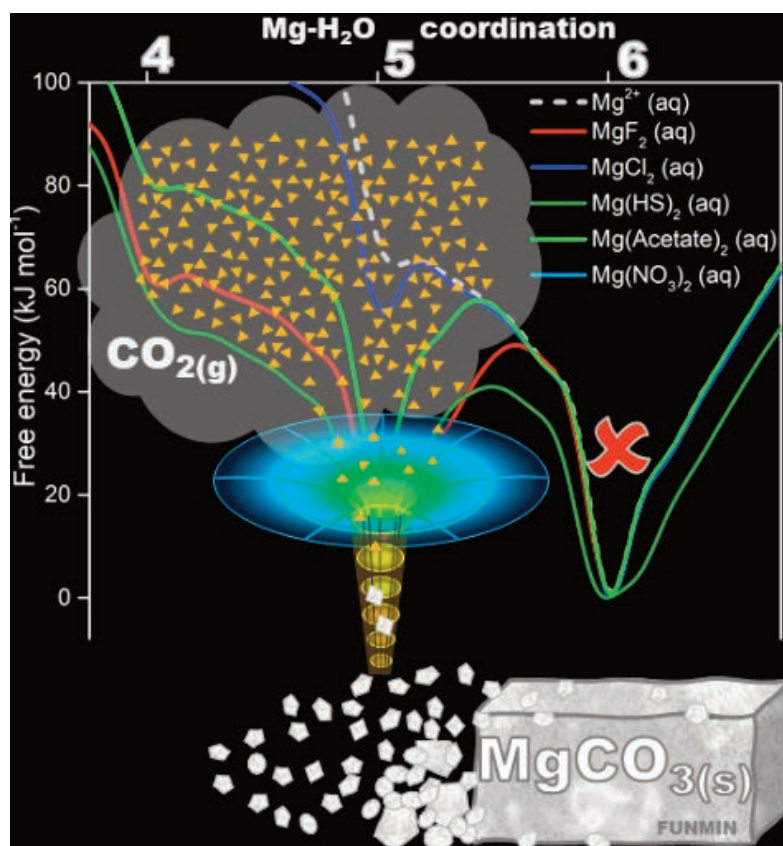


Figure 1 Computer simulations of Mg²⁺ dehydration show that solution additives can stabilise undercoordinated Mg²⁺ hydration configurations, opening coordination sites on Mg²⁺, promoting MgCO₃ nucleation and growth (*CrystEngComm*, 2021, **23**, 4889).

Solution composition can lower the barrier to Mg^{2+} dehydration and subsequent incorporation into the lattice of MgCO_3 , promoting low-temperature crystallisation. Towards tracking experimentally, the CO_2 -to- MgCO_3 conversion, neutron scattering presents unprecedented advantages over traditional techniques for time-resolved *in situ* measurements. However, a setup providing continuous solution circulation to ensure reactant system homogeneity for industrially relevant CO_2 mineralization was currently not available for use on neutron beamlines. We will present the design, construction, testing and implementation of a self-contained reactor rig for use on neutron beamlines at the ISIS neutron source (Rutherford Appleton Laboratories, UK) (**Figure 2**). The assembly successfully accomplished the principal tasks of providing a continuous flow of the reaction mixture for homogeneity, quantitative control of CO_2 flux into the mixture as well as temperature and pressure regulation throughout the reaction and measurements. The design is discussed, with emphasis placed on the reactor including its geometry, components, and all technical specifications. The presentation we also report preliminary work on scaling-up the CO_2 -to- MgCO_3 conversion processes to true bulk (@ 50-100+ L/kg) while controlling carbonate product structures, identities, and properties for their use as fillers/additives in concrete.

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Figure 2 The CO_2 mineralization reactor rig being installed into the sample area of the IRIS beamline at RAL-ISIS. The rig position is adjusted such that the sample cell is aligned with the neutron beam (N) (*Rev. Sci. Instrum.*, 2023, **94**, 093905).

SESSION 2 - ENVIRONMENTAL GEOCHEMISTRY

Conveners:

Maurizio Barbieri (DST, Università La Sapienza), Elisabetta Dore (DSCG, Università di Cagliari),
Nicolas Greggio (BiGeA, Università di Bologna)

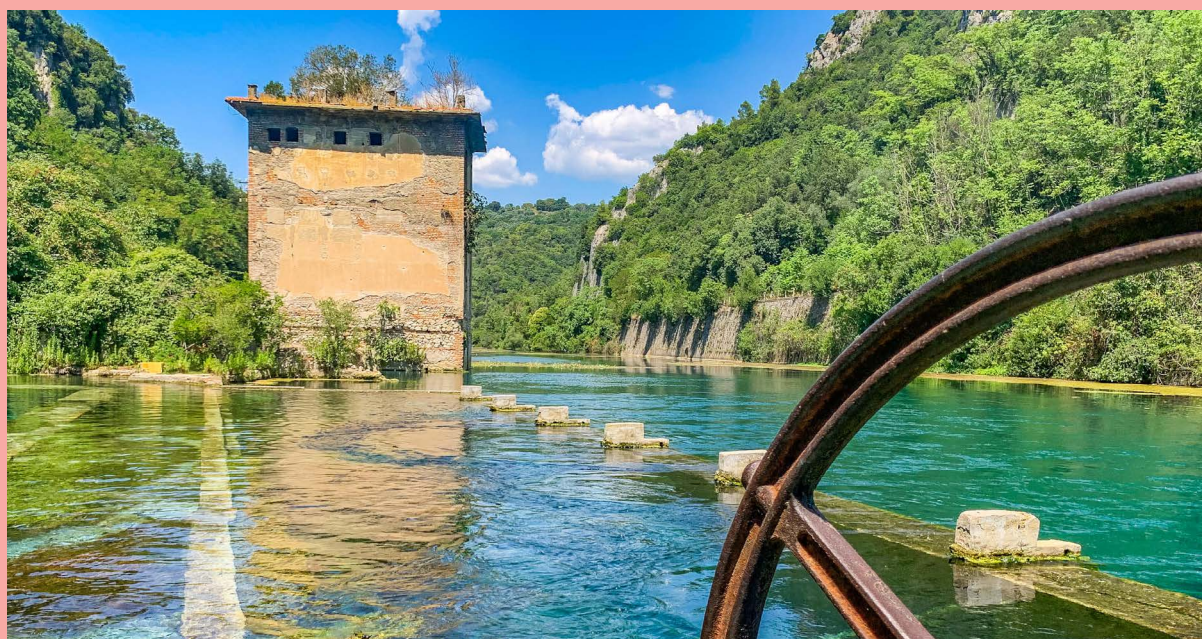


Figure caption: ENVIRONMENTAL GEOCHEMISTRY da blog di @Annalisa Spinosa (le Tre Valigie)

Particulate matter pollution in an Alpine Valley: long-term trends, source apportionment using specific tracers, and the effect persistent inversion dynamics

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Major urban areas in mountain environments are typically located on valley floors. Here, mountain orography drives peculiar atmospheric circulation conditions. Persistent thermal inversion conditions may also occur, strongly affecting air pollution. This study characterizes the particulate matter (PM) pollution in an Alpine valley (Valbelluna, NE Italy) and analyzes the potential effects of local meteorology.

First, long-term trends (2008-2023) are investigated using 3 different approaches to detect the effects of past and recent regulatory efforts at local, regional, and national levels. Since most mitigation measures focused on mobile emissions (e.g., traffic restrictions), the effects of these policies are further evaluated through generalized additive models.

Second, a detailed source apportionment of fine PM ($PM_{2.5}$) in the major city of the valley (Belluno) is performed during a cold season, when higher PM concentrations are observed. Major chemical species and minor/trace elements are analyzed, including specific geochemical tracers for primary biogenic, secondary, and biomass burning aerosols. $PM_{2.5}$ sources are identified and quantified through positive matrix factorization. Results indicate biomass burning as the major source (52% mass), followed by secondary aerosol (21%), biogenic PM (20%), traffic (4%), and resuspension (3%). The source contributions are then handled to account for the local meteorology through dispersion normalization.

Third, the possible effects of persistent thermal inversion events are investigated by assessing the inversion strength from temperature profiles measured at multiple weather stations located at different elevations.

Acknowledgements

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Estimation of Shallow Geothermal Potential for Closed- and Open-Loop systems in the Sibari plain (Calabria, Southern Italy)

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In the framework of the PNRR 2023-2026 project (Tech4You) the estimation and mapping of the shallow geothermal potential of the Calabria Region is currently underway. In this context, this work aims to provide a reliable evaluation of the shallow geothermal potential for exploiting GSHEs (ground-source heat exchangers) coupled with heat pumps for indoor climatization (heating and cooling) in the pilot area of the Sibari Plain. Thermal, geological and hydrogeological data were collected and elaborated by using the methods proposed by [Casasso and Sethi, 2016] (G.POT: Geothermal POTential) and [Munoz et al., 2015] for Closed- and Open-Loop systems, respectively. Preliminary results show that the most suitable area is represented by the central-eastern sector of the plain, where the permeable soils and the shallow piezometric level increase the heat exchange capacity between the subsoil and the geothermal plant. However, direct exploitation of the aquifer by Open-Loop systems implies evaluating possible geochemical or biological issues. Thus, the study of the chemical constituents of the local waters will allow understanding their corrosive hazardousness and the saturation of the main mineralogical phases, which could cause the clogging of the systems. The results will support the decision-making and management phases of future exploitation of geothermal potential and provide important insights into the possible impacts of its intensive exploitation.

Acknowledgements

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The Legacy of Hg Contamination in a Past Mining Area (Tuscany, Italy): Hg Speciation and Health Risk Assessment

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The World Health Organization included mercury among the ten chemicals posing a major public health concern. The mercury-cell manufacturing process has been extensively used in chlor-alkali plants to produce chlorine and caustic soda by electrolysis, representing a potential source for Hg release into the environment. Despite a significant decline due to the membrane cell processing alternative, there is still a use of mercury in chlor-alkali facilities globally. In the Tuscany region (Italy), solution mining by pumping water into NaCl deposits was applied to produce brines for a mercury-cell chlor-alkali plant. The Hg-contaminated exhausted brines were reinjected at depth in the NaCl deposit through *injection* wells, in order to renew the available resources. Activities ceased in 1995 following the dispersion of highly contaminated Hg-bearing brines into the environment, and reclamation started. In the present study, the existing dataset for the pristine soil and water contamination has been evaluated and new data provided. The results indicate the legacy of contamination, with Hg concentration exceeding the regulatory limit in some soil samples. Risk assessment by applying Hg speciation analysis indicates that mercury in soil does not carry a risk of non-cancerous effects for the different exposure routes in case of an outdoor use of the site, but the risk would become unacceptable in case of indoor settings such as residential buildings via vapor intrusion.

Air quality monitoring in environments affected by biogenic, volcanic-hydrothermal and anthropogenic gas emissions: revealing insights using traditional and low-cost techniques

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Air pollution from natural and anthropogenic sources is the primary environmental health risk for 99% of the global population. This study presents the results of a geochemical survey on air quality in areas affected by gas release from different environments: (i) Vulcano Island and (ii) Pozzuoli (southern Italy), where people cohabit with volcanic-hydrothermal gas hazards; (iii) Padule di Fucecchio (northwestern Tuscany), the largest inner wetland of Italy, where the urbanization increase is expected to accelerate the emission of CH₄ and CO₂, and (iv) a CO₂ exploitation facility in Sant'Albino (southern Tuscany). Here, natural and anthropogenic CO₂- and H₂S-rich emissions occur. We employed a strategy that combined (i) low-cost fixed stations to measure CO₂, PM_{2.5}, PM₁₀, and alternatively, H₂S (in hydrothermal and industrial sites) or CH₄ (in the wetland), and (ii) a highly sensitive mobile station to determine CO₂, CH₄, H₂S, and SO₂ concentrations, as well as $\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$, along selected transects. The chemical and isotopic parameters were used to monitor daily variations, revealing trends influenced by the evolution of the Planetary Boundary Layer and local weather conditions, and identify the main sources and processes affecting air quality. Based on the $\delta^{13}\text{C-CO}_2$ values and H₂S/CO₂ ratios, the impact of deep-sourced discharges was clearly detected near the major emissions in Vulcano, Pozzuoli, and Sant'Albino. Moving apart, CO₂ tended to mix, to varying degrees, with background and anthropogenic sources, whilst H₂S exhibited weather-dependent reactivity, rapidly degrading due to oxidation processes in air. The investigated wetland was found to be affected by local anthropogenic CO₂ emissions, with higher concentrations in fall, possibly due to limited photosynthetic activity and increased fossil fuel use for domestic heating. As for CO₂, CH₄ concentrations were slightly higher in the valley floor and showed a biogenic footprint only near the water body.

Mud and water geochemical characterization of the Nirano Mud Volcano (NMV, Fiorano Modenese, Italy)

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Mud volcanoes (MVs) are surface expressions of subsurface processes characterized by movements of large masses of sediments and fluids, called “sedimentary volcanism” due to their morphological resemblance to igneous volcanoes [Martinelli & Judd, 2004, Mazzini & Etiope, 2017]. They are widely diffused and investigated since they are mostly located in petroliferous basins, although studied even by microbiology, geophysics, and structural geology, for their tectonic activity and as earthquake precursors [Martinelli & Judd, 2004]. Geochemical analyses focus mainly on gas composition, indeed, MVs are the second natural source of CH₄ [Sciarra et al., 2019], while mud and water characterizations are almost absent in the literature.

In Italy, MVs occur along the external compressive margins of the Northern (Pede-Appennine margin of Emilia Romagna) and Central Appennine and in Sicily [Candemi & Madonia, 2014, Sciarra et al., 2019]. Nirano mud volcano (NMV) of the Emilia Romagna region is one of the biggest in Italy, situated at the bottom of an oval depression, and the MV lies close to a small anticline in the outcrop of the Plio-Pleistocene “Argille Azzurre” clays [Minissale et al., 2000, Martinelli & Judd, 2004]. The area is characterized by several splatter-type grey gryphons, *i.e.*, individual active vents, whose periodic overflows occur with sufficient frequency to avoid vegetation growth [Minissale et al., 2000, Mazzini & Etiope, 2017]. This work aims to characterize mud and water composition of this mud volcano. Preliminary ICP-MS and IC analyses for major ions (Na, Ca, Mg, K, Cl, NO₃, NO₂, F, PO₃, SO₄) on NMV waters agree with those found by Minissale et al. [2000], with EC of 2.30-15 mS, Cl 418-5370 ppm, and Na 196-3426 ppm, indicating a contribution of both deep fluids and meteoric waters. For mud samples major, minor, and trace element composition will be determined through XRF, ICP-MS, EA-IRMS and stable isotopic (C, and S) analyses.

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Hydrogeochemistry investigations at the Einstein Telescope candidate site of Sardinia (Italy)

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The area near the Sos Enattos former mine (Sardinia, Italy) was selected as one of the candidate sites to host the Einstein Telescope (ET). The European third generation underground interferometric detector of gravitational waves that could be installed in a triangular infrastructure 10 km long sides. The implementation of large-scale underground infrastructures implies deep environmental modification requiring, among the others, detailed geological and hydrogeological evaluation. Moreover, underground activity can significantly impact the environmental conditions at local scale, due to the production of crushed waste rocks that cause a potential risk when these materials, especially in presence of mineralization, are exposed to weathering.

The studied area lies on a crystalline basement made up with micaschist, quartzite, ortogneiss and granitoids rocks. Sulphides mineralizations (mainly ZnS and PbS Ag-rich) are diffuse in the area and were exploited until 1997 at the Sos Enattos mine. Therefore, the knowledge of water-rock interaction (and eventually mineralised bodies) processes is essential for assessing the potential environmental impact of underground works on the quality of waters.

In the framework of the SAR-GRAV and FdS-2021 projects, hydrogeological investigations are being carried out in the area comprised within the potential vertexes limiting the ET triangle and surrounding areas with the aim to evaluate the groundwater baseline conditions. Preliminary hydrogeological surveys were carried out in 2023-24 and twenty-four springs were sampled for both water stable isotopes and chemistry. Stable isotope of groundwater lay close to the SIMWL [Giustini et al., 2016] indicating a meteoric origin of water. Chemistry varied from Cl-Na compositions to Ca-Mg-bicarbonates. In some samples the concentration of Al, Fe, Mn, Mo were found higher than the median concentrations in groundwaters at regional level previously calculated in Sardinian [Dore et al., 2022].

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Threshold and source of nitrate in groundwater. Combined method approach using geochemistry, stable isotopes and statistic tools in the Campidano plain (Sardinia, Italy)

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A combined geochemical, multiple stable isotopes (hydrogen, oxygen, nitrogen, sulphur and boron) and statistical tools approach, were applied to define threshold and potential contamination sources of nitrate (NO₃) in 64 groundwater samples prior to designate new Nitrate Vulnerable Zones [NVZ; EC, 2021] in the Campidano Plain located in southern Sardinia (Italy).

The observed geochemical facies range from calcium bicarbonate to sodium chloride. Concentrations of NO₃ in groundwater occurred in a large range (<1 to 83 mg/L) and the present-day background threshold of NO₃ was estimated at 4.3 mg/L. Concentrations above threshold were mostly originated from manure, sewage, and agricultural activities. Using a Bayesian isotope mixing model and boron isotopic signature, manure and sewage were identified as the predominant sources contributing the highest median value of NO₃. Nitrification, volatilization and denitrification processes were likely to occur at specific sites. Geographic areas showing either a predominant process or a specific NO₃ source were not recognized in the studied area.

Results of the integrated approach applied to the case study in Sardinia, permits to highlight the strengths of integrating geochemical and statistical methods to provide nitrate source identification as a reference by decision makers to remediate and mitigate nitrate contamination in groundwater.

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Potential effects of plastics and nicotine on carbon storage capacity of calcifying marine foraminifera

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Emerging pollutants have become a huge concern for the entire populace due to their critical environmental and human health hazards [Mishra et al., 2023]. The chemical composition of waters and sediments, consequently, the environmental quality and the trophic levels, can be affected by litter and debris such as plastics and smoked cigarette butts (CB) whose associated toxic substances can be bioaccumulated in marine organisms [Araújo and Costa, 2019].

To understand the impact of emerging pollutants on oceans and the interaction with marine organisms, we investigated the effects of plastics, bio-accessible plasticizers (DEHP, bis(2-ethylhexyl) phthalate), CB leachate and synthetic nicotine on selected benthic foraminiferal species by μ -FTIR (Fourier Transform Infrared) spectromicroscopy. We demonstrated that i) nicotine produces cellular stress and induces shell dissolution in *Rosalina globularis*, *Quinqueloculina* spp. and *Textularia agglutinans* [Caridi et al., 2020; Sabbatini et al., 2023]; ii) plastics and DEHP have biochemical effects on the biomineralization process and health status. *Cibicides lobatulus*, *Rosalina bradyi* and *Textularia Bocki*, grown on plastic, showed signals of oxidative stress and protein aggregation. DEHP can be incorporated into the cytoplasm of *R. globularis*, thus entering biogeochemical cycles [Birarda et al., 2021].

We hypothesize that plastic wastes and CB can be sources of secondary pollution besides their presence since their associated additives may produce modifications related to the biomineralization process in foraminifera. This effect would be added to those induced by ocean acidification, which would have negative consequences on the foraminiferal biogenic carbon storage capacity.

Ongoing research focuses on understanding the incorporation of pollutants and modifications in foraminifera shell (e.g., density) by applying Scanning Transmission X-ray Microscopy (STXM) Low Energy X-ray Fluorescence and X-ray computed microtomography.

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Ceramic components in Construction and Demolition Waste: an analysis of their effects on the environment in relation to the new Italian End of Waste directive

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Construction and Demolition Waste (C&DW) unsorted-waste streams are characterized by a strong heterogeneity of materials which can lead to contaminant releases in the environment above the legal limits for recovery [Barbudo et al., 2012]. In the Mediterranean countries, compared to a pure concrete-derived waste stream, the impurities are for the largest part composed of ceramic-based materials. Beside clay bricks, other types of ceramic building materials are usually found and the release of soluble sulphate content and heavy metals seems to be strongly influenced by the amount of them. Furthermore, the presence of residual cement paste can strongly enhance the pH values, which has been proved to promote the leaching process [Englesen et al., 2010]. In this work, several C&DW samples from Ferrara and Perugia (Italy), were analyzed through X-ray fluorescence, inductively coupled plasma mass spectrometry, and X-ray diffraction with Rietveld quantitative phase analysis to assess an in-deep chemo-mineralogical materials characterization. Leaching analyses, following UNI-EN 12457-2: 2004, have been then conducted on pure ceramics samples and on powder mixed with hydrated cement paste (1:1 ratio). The leachate solutions have been analyzed after 24 hours since the start of the leaching. The concentration of contaminant releases is compared with the legal limits that are going to be introduced in Italy in 2024 (End of Waste decree) for the recovery of Recycled Aggregates materials. Our analyses demonstrated that Ferrara C&DW are anomalously enriched in Cr and Ni as Po valley sediments, resulting from the erosion of Alpine and North Apennine ultramafic rocks, are commonly used as raw materials in the building activity. During leaching process, most of them released Cr above the law limits, especially when mixed with concrete. In addition, some samples released also SO₄, indicating the urgency to find a sustainable solution for the C&DW disposal.

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Bulk atmospheric deposition fluxes over Sicily: relative distribution between three different fractions

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Atmospheric deposition samples were collected in different areas in Sicily over two years, using a network of 15 bulk samplers that remained open during the entire sampling period, collecting both wet and dry deposition. After exposure, the collecting systems were rinsed with 150 mL of 2% w/v HNO₃ solution and with 150 mL of pure water (non-solubilised fraction - 1). The rainwater samples were filtered using a 0.45 µm pore size cellulose nitrate membrane and then acidified with HNO₃ (soluble fraction - 2). The filter residue membranes were mineralised through the microwave-assisted method with HNO₃ and H₂O₂ (insoluble fraction - 3). Major (Na, K, Mg, Ca, S) and trace elements (Li, B, Al, Si, Ti, V, Cr, Mn, Fe, Co, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Ba, Pb) concentrations were quantified, for the three different fractions, by an ICP-OES. Atmospheric deposition fluxes were calculated from measured concentrations, rainwater amount and exposure time. For each analysed chemical species, the sum of the contributions of each fraction represents the bulk atmospheric deposition flux. The results showed that the soluble fraction had the highest relative contributions for all major elements, ranging from 72.8% (K⁺) to 94.8% (Na⁺). The highest contributions for Sr (80.7%), Ba (59.7%), and B (59.1%) were also found in this fraction. Copper, Zn, and As had similar contributions in both soluble and insoluble fractions. For all other trace elements, the insoluble fraction had higher relative contributions, ranging from 50.0% (Pb) to 96.7% (Fe and Ti). Notably, the non-solubilised fraction had non-negligible contributions for Pb (39.6%), B (33.0%), Zn (20.6%), and As (20.1%). The study highlights the importance of characterising not only the soluble fraction to avoid underestimates in the deposition calculation. Improvements in the methodology used for studies on atmospheric deposition and its impact on the environment and human health can be derived from these findings.

LucAS project: Evaluation of geochemical-mineralogical background in environmental matrices for the assessment of health risk

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The knowledge about the Pollino Massif reports the presence of asbestiform minerals in rock outcrops, anomalous abundances of Cr, Co, Ni and Pb in soils, and concentrations of Cr(VI) and Ni above threshold values in the aqueous phase. All these features can be a risk factor for the quality of natural resources and the health of resident populations. The LucAS (Lucani per l'Ambiente e la Salute) project aims to determine the geochemical-mineralogical background of chemical elements and target mineral phases and to develop a protocol aimed at estimating geochemical and mineralogical risk. The LucAS project is composed of into two main Tasks: TASK 1 - geochemical mobility, in soil and water matrices, of chemical elements potentially toxic to human health; TASK 2 - Mineralogical, petrographic, and chemical-physical characterization of rocks containing toxic and/or carcinogenic mineral fibres. Specifically, the goal of the project is to develop a protocol of techniques and methods to assess the geochemical background of soils and the distribution of heavy metals, particularly Cr(VI), in surface and groundwater in the Seluci pilot area in the Municipality of Lauria (Potenza). In this area, soils are characterized by potential environmental hazard since are developed on mafic and ultramafic rocks rich in minerals containing heavy metals such as Cr, Ni, Pb and Co. In detail, in the solid matrix, the mineralogical risk due to the presence of asbestiform minerals, such as tremolite, will be assessed and the possible geochemical risk associated with heavy metals will be estimated. The concentration of Cr, Co, Ni and Pb will be determined in the aqueous phase. These activities, together with the definition of the geochemical background and related risk, will support regional decision-making working in the field of environmental resource protection and management for the possible integration and/or modification of current regulations.

Application of chemical quality trends over time and space as a tool to evaluate river geochemical evolution and contamination

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A correct water management represents one of the main challenges that humanity must face in the next future. We propose a new approach that aims to assess the quality and quantify the environmental impact of different compounds in surface waters over space and time by applying the Chemical Water Quality Index (CWQI; Chemeri et al., 2023), which is only computed considering the main chemical parameters. This method aims to (a) assess the water quality evolution along the river courses; (b) evaluate the contribution of different elements and compounds in influencing and compromising water quality; (c) detect contaminated areas; (d) unravel how water quality has changed in response to environmental laws and mitigation actions. To test the feasibility of the proposed method, a pilot study was conducted in the Arno River (AR) basin (Tuscany, Italy). The AR flows for 242 km through areas characterized by a relatively strong anthropogenic pressure due to the presence of large cities (e.g., Florence, Pisa) and widespread industrial and agricultural activities. Previously published data on the riverine geochemistry from selected sites (11 from the main course and 8 from the main tributaries), referred to four different sampling periods prior (1988-1989, 1996-1997, 2002-2003) and after the implementation of the EU Water Framework Directive (2017), were taken into account. The CWQI clearly evidenced that the AR is characterized by a good to medium quality (CWQI<2.5) for the first ca. 130 km, with a clear quality deterioration that occurs downstream of Florence, due to the increasing anthropogenic load along the main catchment. Chloride, sodium, and secondarily, sulphate were recognized as the main species compromising water quality in the four temporal frames. In almost 30 years, no significant improvements were recognized since the same contaminants abundances and environmental impacts were detected, indicating a poor attention has been paid with respect to the anthropogenic pressure operating in the AR.

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An interdisciplinary approach in environmental studies: the RES2OX project - Investigating Specialized Metabolism as an integral factor to improve oxidative stress resilience in native plants exposed to metalloids naturally contaminated soils

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Human activities, industrialization, and modern agricultural practices are mainly responsible for the increase in soil contamination by potentially toxic elements, like arsenic. In addition, natural sources contribute about 1/3 of the total annual release of As to the atmosphere and most of this comes from volcanoes. The presence of As in soils affects the plant cycle giving rise to oxidative stress exerted by reactive oxygen species (ROS), such as hydroxyl radicals, superoxide radicals, and H-peroxide. Recent in vivo studies conducted using metabolome and transcriptome profiling of the model species confirmed the role of flavonoids in the enhancement of oxidative tolerance. Flavonoid function remains to be determined experimentally in naturally tolerant wild plants living in stressful soils. Soils developed on the volcanic substrate, as a considerable part of the Campanian region and Etna surroundings, are rich in neo-formed amorphous aluminosilicates and organo-mineral compounds and have a high binding capacity for trace elements, such as As. Significant tolerance to As-rich soils was shown for *Brassica rapa* subsp. *sylvestris*, a species widely spread in southern Italy including in volcanic substrates. However, the role of flavonoids in the oxidative stress tolerance in *B. rapa* remains to be addressed, although the tolerance mechanisms, as adaptive traits evolved in this species, can become a knowledge milestone for future phytoremediation. Through novel untargeted transcriptome and metabolome approaches is now possible, also for non-model species, identify, with unprecedented precision, all the metabolites and expressed transcripts produced by the plant in response to a stress treatment. Therefore, in the present project, we are investigating the role of flavonoids as ROS scavengers, within the tolerance strategy of wild *B. rapa* naturally growing in soils affected by As, by performing transcriptome and metabolome profiling analyses.

Identification of anthropogenic and geogenic contributions of trace metal(loid)s in coastal sediments through a geochemical normalisation approach based on regional background values (Gulf of Trieste, northern Adriatic Sea)

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Metal(loid) concentrations in coastal sediments are often due to the contribution of anthropogenic inputs to the site-specific natural geochemical characteristics of the investigated area. The aim of this study was to assess the origin (geogenic or anthropogenic) of metal(loid)s in the surface sediments of the eastern sector of the Gulf of Trieste. Aluminum was identified as an ideal proxy element due to its excellent correlation with the muddy fraction. The common origin of the elements was confirmed by the positive correlation found among correlated groups of elements such as Pb, Cu, Zn and Mo, on the one hand, and Tl, Li, Cr, Mn and Ni on the other. The comparison with the environmental quality standards (SQA-MA) defined by current legislation (Legislative Decree 172/2015) showed that threshold levels were exceeded for Cr (100%), Ni (95%), Hg (87%), Pb (84%), As (74%) and Cd (5%). Since the SQA-MA values do not take into account the natural site-specific geochemical features of sediments, a normalisation procedure was applied to quantify the real anomaly. Regional functions for metal(loid)s were determined using sediments from a core collected in the central sector of the Gulf as a baseline [Covelli et al., 2006] in order to subsequently calculate enrichment factors (EFs). Negligible or low contamination was found for sediments far from the urbanised and industrialised areas, whereas the EFs were higher near the coast, revealing, in some cases, significant isolated anomalies; the highest enrichment was found for Hg, whose average EF value was 14 times higher than the local baseline. The highest EFs were found for Cu (10.7), Cd (8.9), Mo (7.8), Pb (7.2) and Zn (5.6). Chromium and Ni, on the contrary, which show high concentrations, are actually not enriched. This is due to the effectively lithogenic nature of these two elements, which are present in the sediments of the Gulf of Trieste in relation to the peculiar mineralogical characteristics of the area.

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Soil background values at abandoned mining areas in the Paleozoic “Metallifero Region”, SouthWest of Sardinia

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The Regional Authority of Sardinia commissioned ARPAS to perform the survey regarding the “Determination of background values in soils and groundwater of abandoned mine areas in Sardinia”. The project, planned and driven by ARPAS with the contribution of University of Cagliari, regards 151 abandoned mine sites, which constitute important sources of metals and metalloids contamination and hazards. The occurrence of mining sites, their location and characteristics depends on the evolution of at least 4 major period of mineralization recognized from Paleozoic to the Tertiary age. On the base of the main paragenesis and mineralization settings were reassembled 55 ZONES with consistent data, developing specific conceptual models. The most important mining area lies in the SW-Sardinia in the so kwon “Metallifero Region”, Paleozoic basement, in which the mineralization style is the “Mississippi Valley Type”, carrying Pb-Zn-Cd sulphides and oxides, mainly hosted in metacarbonates of Cambrian age. This work presents preliminary results for the soil background, in an area of 300 square kms, involving 50 abandoned mines of various sizes, one third of the abandoned mines in Sardinia, where 1400 soil samples were collected and analyzed.

As expected, the high values content of metals and metalloids largely exceed the exploited mining area, causing widespread occurrence of possible concerning natural contamination. The earliest evaluation regarding the metacarbonates parent rock, returned background values, for instance, in Pb-Zn-Cd, up to two order of magnitude above the Italian regulatory standards for soils. The scheduled project target in 2024 is to collect analyze and evaluate more than 2500 surficial soil samples by completing the 55 ZONES.

The evaluated background values and their distribution is collected in an “Atlas of Background Values” on a CLOUD platform, based on a database exceeding 150.000 data. At the end of the project, the Atlas will be available for the stakeholders with a specific WEBGIS application in the Regional informative system.

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Multidisciplinary hydrogeochemical and isotopic assessment of the Pordenone Plain (Northeastern Italy)

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This study aims to characterize the hydro-geochemical and isotopic features of the complex groundwater system in the Pordenone Plain (northeastern Italy). The area is an important industrial and agricultural area exposed to severe anthropogenic pressure and climate change, which put its water resources at risk in terms of quantity and quality, making it of high scientific and social interest. The hydrogeological setting of the Pordenone Plain has been previously simplified as an unconfined continuous aquifer in the High Plain that changes into a multilayered confined aquifers system towards the Low Plain. However, this study reveals significant lithological and structural heterogeneities in the High Plain that exert a strong influence on its subsurface hydrodynamics. All waters exhibit a Ca(Mg)-HCO₃ composition with relatively high Na-K values in the aquifers of the Low Plain related to cation exchange processes. Water stable isotopes and tritium analysis provide evidence of two distinct recharge areas and different average residence times of waters within the aquifers. Three different groundwater flows have been identified and reported in a comprehensive hydrogeochemical conceptual model of the plain. In detail, the shallower flow is represented by the unconfined and semi-confined aquifers of the High Plain hosted in gravelly sediments and recharged by local precipitations. The intermediate flow fed by the pedemontane recharge area, includes unconfined deep aquifers of the High Plain, semi-confined/shallow aquifers of the resurgence belt area and karst springs of the eastern pedemontane zone and it's characterized by relatively low residence times. The deeper flow, fed by the Alpine recharge and characterized by prolonged residence times, is represented by the deep confined aquifers of the Low Plain. The chemical and isotopic variability of the studied waters represent valuable insights for the sustainable management of groundwater resources in the Pordenone Plain.

Investigating the origin of carbon and sulfur volatile compounds in areas affected by hydrothermal emissions and anthropogenic activities: the case study of Tivoli Terme (Central Italy)

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Hydrothermal discharges are regarded to be important sources of volatiles that may affect local air quality. Based on compositional and isotopic data, a geochemical survey aimed to trace the origin of carbon (CO₂ and CH₄) and sulfur (H₂S and SO₂) volatile compounds, and to understand the role that weather conditions and chemical reactions play in determining their occurrence in air, was carried out in the area of Tivoli Terme (Rome, Central Italy), where different natural and anthropogenic sources coexist.

The daily variations of the species in air were controlled by the evolution of the Planetary Boundary Layer, as well as weather conditions favoring their transport or degradation. Keeling plot analysis on CO₂ revealed the presence of three main sources mixing at different degrees: (i) the hydrothermal emissions, which contributed significantly to the local atmospheric CO₂ composition when wind blew from the north sector of Regina and Colonnelle hydrothermal lakes; (ii) the limestone (travertine) mining activity occurring at east, associated with CO₂ isotopic footprint up to +5 ‰ vs. V-PDB during rain events; and (iii) traditional anthropogenic sources related to fossil fuel combustion. While CO₂ from these sources simply mixed with atmospheric background, H₂S, whose provenience was ascribed to (i) the hydrothermal emissions (associated with lower CO₂ concentrations, heavier $\delta^{13}\text{C-CO}_2$ values, and higher CO₂/CH₄ ratios) and (ii) a paper mill located eastward to the study area (associated with higher CO₂ concentrations, lighter $\delta^{13}\text{C-CO}_2$ values, and lower CO₂/CH₄ ratios), was significantly affected by photochemical degradation due to oxidation processes, leading to the production of SO₂ as already observed in other hydrothermal areas. The highest concentrations of CH₄ were mainly ascribed to a thermogenic origin, though a contribution from the landfill and the agricultural activities southward was not to be completely excluded.

A comparison of traditional and innovative tools for the geochemical characterisation of surface waters: the case study of the Serchio River Basin (northern Tuscany)

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Rivers are complex systems undergoing multiple stressors (natural and anthropogenic), and controlled by self-organization, multi-scale variability, hydraulic and topographic gradients, as well as dissipation (Kleidon et al., 2013). This high heterogeneity requires the development of innovative and holistic strategies able to capture the collective behavior of the system on different spatial and temporal scales. Compositional Data Analysis (CoDA) theory offers proper tools to look at the whole and catch the multi-variability and mutual interactions that characterize the life of complex systems. However, the construction of an extensive multi-level database, allowing to relate the behavior of different potential environmental drivers (e.g., climate, lithology, slope) to the geochemical composition of riverine waters, is a fundamental step to identify the resilience of these natural resources to change. In this study, sponsored by the National Centre for HPC, Big data and Quantum Computing of the PNRR, we selected the Serchio River Basin (Tuscany) as a pilot area due to the heterogeneity of both lithological (sedimentary formations alternated with metamorphic units) and anthropogenic sources (agriculture, paper mills, mining activities, urbanization) affecting the catchment evolution. While a multi-level database is under construction, the composition of river waters collected during the first monitoring period in February 2024 was preliminarily investigated employing both traditional geochemical representations and new CoDA statistical tools. The aim was to identify compositional indices to efficiently monitor the state of the investigated system to be linked to other environmental variables. To gain first information about the processes that control compositional changes and to orient the subsequent sampling campaigns and the building up of the multi-level database, the obtained results were also compared with the distribution of some thermodynamical parameters.

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Air quality assessment using a multi-instrumental and low-cost approach: a case study of the Greve River basin (Chianti territory, central Italy)

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Traditional multi-instrumental integrated systems for the monitoring of air quality rely on fixed station networks, which have limitations in terms of spatial coverage, frequency of data acquisition and costs. To address these challenges, low-cost technologies recently offer a solution for wide-resolution monitoring and real-time exposure control.

In this study, an air quality survey was carried out in the Greve River Basin (Central Italy), employing two different approaches: (i) a mobile station equipped with a Picarro analyzer for CO₂ and CH₄ concentrations and isotopic values, and (ii) continuous monitoring of CO₂, CH₄ and PM concentrations at five fixed sites using low-cost stations (LCS). This survey was complemented by atmospheric deposition samplers to gather particulate samples for laboratory analysis. Results from both approaches were similar, indicating higher CO₂ and CH₄ concentrations downstream in the most densely urbanized area of the Greve River Basin, ascribed mainly to vehicular traffic based on their isotopic signature. Spatial and temporal behavior of air contaminants reflected the evolution of the atmospheric boundary layer that favored relatively high pollution during nighttime and early morning when more atmospheric stability occurred. PM patterns were similar to those of gaseous species, suggesting common sources (related to traffic or agricultural activities), clearly recognized based on the chemical composition of the atmospheric deposition in the collection sites.

The high spatiotemporal resolution of data acquisition provided by the LCS represents an important advance for the development of new monitoring networks, complementing traditional instrumentations.

Risk analysis in alluvial soils contaminated by mercury from historical mining activities through metal speciation: a comparison between thermo-desorption and selective sequential extraction

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Mercury (Hg) is recognised as a global pollutant occurring under various forms in the environment, each characterised by different mobility and bioavailability. Thus, determination of Hg speciation in environmental samples is essential for a proper evaluation of Hg pollution impact and potential associated health risk. Selective sequential extraction (SSE) techniques are usually used to assess Hg speciation in soils, but this approach is usually time-consuming and suffers of low reproducibility of results [Issaro et al., 2009]. An alternative option to SSE may be represented by thermo-desorption (TD), which allows a simple discrimination of Hg occurring as non-mobile red cinnabar (α -HgS) thanks to its specific release peak temperature. In this study, the application of TD for health risk assessment was tested in some sites within the Isonzo alluvial plain, impacted by past mining activity at upstream Idrija Hg mine [Acquavita et al., 2022]. Potential risk associated with Hg volatilisation, leaching and ingestion was modelled considering the average amount of non-cinnabar (non- α -Hgs) fraction determined on all available soil samples. Results were compared with those obtained through SSE approach [Bloom et al., 2003]. Due to contamination from mining, in all samples α -HgS was the predominant fraction. Overall, TD overestimated the risk associated with volatile and soluble fractions of Hg compared to SSE. Conversely, comparable and acceptable risk (hazard index <1) was obtained for ingestion pathway through both techniques. However, TD allows to analyse a higher number of samples than SSE in less time, resulting in an increased representativeness of real situation. Considering also the good reproducibility of the results, TD can thus represent a valuable tool for a first screening of potential health risk at Hg contaminated sites, possibly coupled with simple single-step extractions for the determination only of soluble Hg fraction.

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Dissolved load in the Chirchik and Akhangaran river basins (Uzbekistan, Central Asia): Natural and anthropic inputs

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The understanding of the sources of dissolved load influencing water chemistry is a critical step to ensure water safety and effective water management. In Central Asia, Uzbekistan experiences water scarcity and water stress, being highly dependent on external flow from the upstream water-rich neighboring countries. In this study, the major ion chemistry and trace element data were obtained on surface- and groundwater collected during a survey in October 2023, from the Chirchik-Akhangaran river basins, in the Tashkent province (Uzbekistan). These rivers are of great importance to industry, agriculture, and household water supply, and their water resources are intensively used for hydropower production, industry, and crop irrigation, causing the river flow to decrease rapidly.

The aim was to investigate the geogenic and anthropogenic contributions to the dissolved load, with implications for water quality and management plans.

The results indicate that the geochemistry of waters from the upstream Akhangaran-Chirchik catchments reflect silicate and carbonate rock weathering. The downstream increase in Na^+ , K^+ , SO_4^{2-} , Cl^- , and NO_3^- reflects anthropogenic pressure from the use of fertilizers in crop production and manure spreading. Nevertheless, the common water quality indices (SAR, $\text{Na}\%$, and KI) indicate that most river waters are suitable for irrigation purposes. The concentration of potentially toxic elements in most waters is lower than the thresholds set for water quality by different regulations. An exception is the water in a coal fly-ash pond related to the Angren coal-fired power plants, showing exceedingly high As, Al, B, Mo, and Sb concentrations due to leaching of contaminants from the coal fly-ash, with possible groundwater impacts associated with infiltration. Although the effects of seasonal changes and irrigation periods on water quality require further investigations, the results obtained are suitable indicators for water resource management.

Geochemical assessment of river and stream sediments in the Chirchik-Akhangaran river basin (Uzbekistan, Central Asia)

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The geochemistry of river and stream sediments depends on several factors, including the nature of exposed lithologies in the source area; the weathering and erosion rates, also driven by climate changes; the different grain-size and sorting due to hydraulics and sediment dynamics; recycling processes and anthropogenic inputs. In particular, the response to post-depositional weathering depends on sediment mineralogical composition, since some mineral decomposes chemically and mechanically relatively swiftly, while others are more stable retaining certain elements. Trace elements, including potentially toxic elements (PTEs), from river and stream sediments can enter the aquatic ecosystem, affecting water quality, and may both concentrate in the detrital fraction or be adsorbed on the surface of the clay-size fine-grained fraction. In the Chirchik-Akhangaran basin (CAB) in the Tashkent Province of Uzbekistan (Central Asia), little is still known about the dominant geogenic and/or anthropogenic sediment sources in rivers and streams. In the present study, stream and river sediments were collected in 21 sampling stations in the CAB upstream catchments and floodplain, and the grain-size control on trace element geochemistry was investigated. Some of the observed geochemical patterns are attributable to the different contribution from geogenic sources; however, enrichments in some trace elements such as Zn, Cu, Ni, Cd, and Pb, in particular in the Akhangaran catchment, are attributable to the increasing of elements from mining activities and/or weathering of mineralized rocks entering waterways. The comparison with freshwater sediment quality guidelines TEC (Threshold Effect concentrations) and PEC (Probable Effect Concentrations) indicates potential threats for aquatic biota, in particular for As, in both the Chirchik and Akhangaran river systems. The possible anthropogenic contribution is highlighted by indices such as the Geoaccumulation Index and Contamination Factor.

The use of water isotopes as environmental tracers in contamination phenomena between aquifers and leachate in municipal solid waste landfills

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Nowadays, one of the serious environmental threats is groundwater contamination, due to leachate from municipal solid waste landfills. In recent years, stable isotopes have been used as environmental tracers to identify potential groundwater contamination, since they can be used to determine sources, pathways, and timescales of environmental processes. Deuterium (^2H) and oxygen (^{18}O) isotopes have been successfully applied to determine contamination phenomena, when groundwater interacts with leachate. In these cases, groundwater presents an enrichment of $\delta^2\text{H}$, probably caused by methanogenesis processes, in which bacteria preferentially use the “lighter” isotope of hydrogen (^1H); thus, the remaining hydrogen is enriched in ^2H , the “heavier” isotope, without producing a proportional increase in ^{18}O . The deuterium excess (d-excess) influences the isotopic content of deuterium and oxygen¹⁸ and can be used to identify processes occurring under non-equilibrium conditions. An index F has been set up as a percentage change in d-excess, given by the ratio between the d-excess for samples' d-excess reference value. This allows the definition of a system of three alert levels to evaluate and control the contamination of aquifers by leachate. F index values higher than 1.1 highlight possible phenomena of aquifer contamination due to leachate. The case study's data on isotopic analyses of ^{18}O , ^2H , and ^3H indicate a leachate and groundwater mixing phenomenon. The influence of this mixing phenomenon determines a reduction in the ORP redox potential in groundwater, which takes on low and sometimes negative values. This condition creates anaerobic environments and reduces conditions that favor the mobilization of metals, such as Mn, in groundwater, which can reach concentrations higher than legal limits. Therefore, in the study area, the overlap of these two phenomena seems evident, such as causing the deterioration of groundwater.

Short and long term chemical variations at lake Trasimeno (Italy)

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Lake Trasimeno (Italy) is a shallow, endorheic lake with a high salinity of lake water. Temperature, pH, chemical and isotopic composition are characterized by seasonal variations strictly related to fluctuations in water level, precipitation and evaporation [Ludovisi and Gaino, 2010; Frondini et al., 2019]. These seasonal variations are superimposed on a long-term trend of salinization and warming that caused an increase of temperature of about 1.3°C and an increase of salinity from 400 to more than 1000 mg/L in the last 50 years. The salinization trend is accompanied by a progressive change in chemical composition with an increase in mobile species (Na, Cl). Recent salinity data suggest that the warming/salinization trend is not linear but is accelerating, following the increase in land surface air temperature (LSAT) that has occurred over the past 50 years of global warming.

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Long term geochemical evolution of groundwater in Umbria (Italy)

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The Environmental Protection Agency of Umbria (ARPA-Umbria) has been conducting the quantitative and quality monitoring of regional aquifers since 1998 through a network of about 250 sampling points. From 1998 to the present day, two to four measurement campaigns per year have been carried out. Together, the analyses constitute a database of more than 10,000 samples distributed over a 25-year period, providing an exceptional tool for assessing the long term trends related to both local and global factors, such as climate change. For each sample the field determinations (T, pH, electrical conductivity, Eh, dissolved oxygen, alkalinity) and the analyses of the major ions, phosphorous and nitrogen species, trace metals, hydrocarbons, polycyclic aromatic hydrocarbons, organic solvents, pesticides and herbicides are available. The entire dataset, encompassing both the full range of aquifers and individual aquifers, yields intriguing findings regarding parameters associated with carbonate systems. During the designated time period, pH, alkalinity, as labile parameters, or ionic strength, and the solution's saturation index of calcite, exhibited discernible lowering.

Geochemical characterization of marine sediments from a maritime area around Elba-Argentario Basin (Tyrrhenian Sea, Italy)

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We present the first results, focused on the bottom sediment geochemistry, of SeaGMA project aimed at acquiring geochemical and microbiological samples at the seafloor along the Italian borders by sampling of bottom sediments and seawaters on a regular grid. This study regards samples from the northern-central Tyrrhenian Sea between the Arno river mouth and the Argentario Promontory.

The sediment samples were collected using a box corer with an average stratigraphic resolution of about 20 cm. Surface sediments (n=99) were prepared for analysis by washing an aliquot with deionized water to remove interstitial seawater. In combination with the marine samples, we collected sediments from the major rivers draining to the studied marine area to constrain provenance signal at sea-land transition. The analytical effort included X-Ray fluorescence spectrometry in combination with gravimetric analysis for the evaluation of volatile content and the aqua-regia digestion of selected samples followed by ICP-MS analyses.

Data analysis considered some geochemical indexes useful to characterize local sediment provenance signals, supported by the results on river sediments. Based on these analyses three major areas were recognized:

- a. a wide population that included fine grained samples with relatively high concentrations of As, Cr, Cu, Zn and others that can be related to a contribution from the Plio-Quaternary volcanic rocks outcropping in southern Tuscany and Latium (e.g. Ba, Nb, Th, Y).
- b. The second population mostly includes sampling sites to the North of Elba Island with an exception to the Southwest. This population showed high contents in carbonate and a geochemical signal that suggests a clear contribution from the ophiolitic rocks outcropping inland.
- c. A third small population includes some of the westernmost stations between the Islands of Capraia, Elba and Montecristo. These samples showed high CaO content and extreme Sr concentrations (up to 4700 mg/kg).

Application of membrane processes to purify Cr-rich groundwaters in Pollino Massif area (Southern Italy)

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Ophiolite areas represent peculiar sites which can be studied from a different scientific point of view. In the environmental field, several issues like the presence of fibers in air and/or waters as well as the release of pollutants into groundwaters, represent the topics most widely discussed. Among different pollutants, chromium in its hexavalent form represents a dangerous element which exceeds the critical threshold in these geological settings [Apollaro et al., 2019]. Chromium levels can be enriched into soil and groundwaters as a result of water-rock interaction processes, becoming a threat for the ecosystem and human health. In the frame of the PNRR project (CUP B83C22003980006), a detailed geochemical survey was performed in the ophiolitic areas of Pollino Massif (Southern Italy) to acquire geochemical information about groundwater interacting with these kinds of rocks. The geochemical mapping allows the selection of polluted waters and the setting of laboratory treatment tests by using membrane processes [Fuoco et al., 2020]. The main scope is selecting the best operative performance in the laboratory to develop a scale-up of membrane plant in the field. The production of decontaminated water as a final product for drinking or irrigation use is the main challenge of this project.

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PTEs in river ecosystems: exploring their natural and anthropogenic sources in the Ombrone Grossetano River Basin (OGRB, Italy)

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Although living organisms need varying quantities of specific Potentially Toxic Elements (PTEs) (such as Fe and Zn) for their development, their accumulation in river ecosystems can disrupt biota equilibrium. As PTEs originate from both natural processes (e.g. rock weathering) and human activities (e.g. industrial), geochemical tools able to discern their sources are crucial to gain insights into the ecological and geological interplay.

This study focuses on the main sources of PTEs and their potential effects on the aquatic ecosystems in the Ombrone Grossetano River Basin (OGRB, Italy), which was selected as a pilot area due to specific features, including: i) lithological heterogeneity; ii) predominant agricultural land use; iii) presence of abandoned mining sites and protected natural areas; iv) thermo-mineral water inputs and seawater intrusion. Surface waters and suspended solids (sampled under diverse discharge conditions), together with sediments, have been or are about to be analysed in terms of major, minor, nutrients, trace elements and PTEs.

Stream waters display a wide chemical variability: from Ca(Mg)-HCO_3 to $\text{Ca(Mg)-SO}_4(\text{Cl})$ and Na-Cl , along with local enrichments in Mn, Co, Ni, Cu and Zn, due to both diversified water-rock interaction processes and natural (e.g. seawater intrusion) and anthropogenic (e.g. agricultural runoff) stressors.

PTEs content in sediments can be primarily associated with the lithological features within the sub-basins, the presence of ore deposits and past mining activities

As a key point of this survey is to understand the provenance of PTEs, ongoing analysis of stable and radiogenic isotopes (C and Sr in all three matrices; N, S, Nd and Pb in suspended solids and sediments) will be used to better constrain the sources of these elements. Biodiversity evaluation will also be pivotal to link abiotic and biotic components of the ecosystem and achieved via innovative monitoring techniques such as eDNA and eRNA sequential analysis.

Geochemical characterization of the recent deposits from the May 2023 Romagna flood and comparison with local deeper deposits

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The Emilia-Romagna flood event of May 2023 was widespread, affecting 19 river basins, and characterized by intensity levels with a return period of more than 500 years, as reported by the Commission of Experts appointed by the regional government. Several riverbanks collapsed and large areas were flooded resulting in a sediment deposit covering the local active soils with variable thickness, ranging from a few centimeters to almost 1 meter.

Before the construction of riverbanks lowland areas experienced frequent flooding and the continuous deposition of new material was commonplace. Fortunately, human intervention prevented flooding episodes and the deposition of new material over active soil. Consequently, the flooding event of last year provided an opportunity to sample and characterize recent flood deposits as well as deeper (older) sediments, enabling a geochemical comparison.

Fifteen sampling locations were identified corresponding to main riverbank failures along seven rivers. Four samples (each 0.2 m deep, from 0 to -0.8 m) and one sample representing recent flood deposits were collected at each site using auger coring equipment. X-Ray Fluorescence Spectroscopy (XRF) and Thermogravimetric Analysis were performed on the solid samples to determine total major and trace elements content and LOI, respectively.

The flood deposits revealed inter-basin geochemical variations. Higher levels of SiO_2 and Al_2O_3 were observed in the Reno river tributaries (Rrt: Sillaro, Santerno, and Senio), while they were lower in the Romagna rivers (Ror: Lamone, Montone, Ronco, and Savio). Conversely, LOI and CaO exhibited the opposite trend. The abundance of trace elements effectively distinguished between Rrt and Ror sediments, with the former generally enriched in As, Ba, Co, Cr, Cu, Ni, Pb, V, and Zn, and the latter enriched in Sr and U. No differences are evident when comparing recent flood deposits with the deeper sediment. The most significant finding was the higher S content in recent deposits compared to the ancient ones across all locations. Additionally, the higher LOI content in recent deposits from Ror, results in increased concentrations of Fe, Mg, K, Cr, Ni, Rb, V, and Zn compared to the ancient material. Among the analysed trace elements none exceed legislative thresholds except V in Rrt deposits, but it is well known that background values of the V are elevated in the area.

Geochemical characterisation of 'road dust' in the urban area of Ravenna (Italy)

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Road dust is a mixture of particles that are deposited on the road surface and contains inorganic and organic constituents sourced by vehicle exhaust, tire wear, brake-lining wear, road surface abrasions, soil dust, vegetative detritus, and atmospheric fallout [1]. Therefore, road dust acts as a sink of pollutants originated from anthropogenic sources and Potential Toxic Elements (PTEs) are the most relevant among the inorganic. Once deposited, road dust may become part of the airborne particulate matter in dry period exposing human to its inhalation, ingestion, and dermal contact [2]. While, in wet season rain physically wash the road and runoff may transport particles or solubilize PTEs moving from road dust to drain canals up to water bodied, and consequently causing various ecological risks [3].

The Ravenna area presents a complex mosaic of land uses ranging from natural, touristic and agricultural to industrial destinations. The harbour and associated industrial activities significantly contribute to road transportation, while rail transportation remains relatively modest. A vast network of roads surrounds the harbour and its associated industrial zone, providing access not only to the industrial area but also to the city and coastline. In autumn 2023, concentric sampling activities were conducted, meticulously collecting road dust samples from three different rings located 0.5, 1, and 4 km away from the core of the industrial area. Sixteen dust samples have been collected, sieved < 180 micron and prepared for X-Ray Fluorescence Spectroscopy (XRF) to determine total major and trace elements content.

Results have been compared with local surface soil samples to identify geochemical differences. Among the analysed trace elements Cr, Cu, Sn and Zn, several locations exceed legislative threshold with Zn exceeding 150 µg/kg in 13 out of 16 samples reaching a maximum concentration of 800 µg/kg. Road dusts are enriched in Ca, Mg, LOI and P compared to neighbouring surficial soils. Ca and Mg originate from carbonate substrate present in asphalt, P derives from organic matter from adjacent vegetation while LOI contains organic matter from wood and leaves, asphalt binder, abrasion of tires and plastic material. Among trace elements Zn serves as the main indicator of tire abrasion, being constituent of the rubber. Cu and S come from brake consumption with the later also originating from SO_x emission. The road dust samples from the industrial site do not show particular abundance in trace elements; conversely, the most enriched samples are found on the heaviest roads.

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Total alpha and beta activities and Rn-222 concentrations in the water supply system of Campania region: How safe is tap water?

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Besides direct environmental exposure, humans can be internally exposed to ionizing radiation through ingestion and inhalation of food, including liquids. Considering the daily consumption of drinking water, the assessment of the radiation dose received by people through its ingestion or inhalation can be regarded as, with good reason, a topic of great scientific and public health interest. To explore this topic, total alpha and beta activities and Rn-222 concentrations were determined in water from different sections of seven aqueducts belonging to the water supply system of Campania region, known worldwide for its volcanism. The study highlights the variability of alpha and beta activities, and Rn-222 concentrations in water supply system, which is influenced by several factors, including the composition of the rock constituting the groundwater reservoirs, the mixing process of waters from different origins, the building materials of the aqueducts, and the integrity of the infrastructure. Guidelines proposed by Italian and international regulation entities were considered to determine if total alpha and beta activities and Rn-222 concentrations found at the taps of the different aqueducts should be considered detrimental to public health. Based on a deterministic and a stochastic approach, a health risk assessment was also tested for Rn-222, assuming direct ingestion and showering as potential exposure pathways. Results showed that applying guidelines returned an absence of hazard, whereas risk assessment returned a high probability of exposure to unacceptable Rn-222 doses for some aqueducts. Beyond the usefulness of obtained results to plan actions to improve the safety of drinking water in Campania, our outcomes represent a warning for bodies dealing with public health at any level: the use of guidelines can bring an underestimation of the risks exerted by the exposure to Rn-222 on human health. Further, using a probabilistic approach in risk assessment accounting for uncertainty can favour risk forecasts based on more “realistic” scenarios.

Classification and hydro-geochemistry of karst springs along the southern coast of Albania

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The southern Albania coast, about 147 km long, represents one of the fastest growing areas of the country for tourism and local economy, resulting in serious problems concerning water supply. Due to the karst nature of the territory, groundwater represents the only freshwater resource for locals; even though large volumes of water flows throughout the aquifers, human activity and climate change effects threat this underground resource.

The aim of this research is to describe both the main factors influencing the karst groundwater quantity and quality, and the drainage characters of the study area. Based on the different geological-structural conditions and the stage of karst processes development, drainage occurs in different ways; five main drainage types can be distinguished along the Southern Albanian coast: (a) overflowing springs, (b) descending springs, (c) coastal springs, (d) submarine spring, and (e) diffuse drainage. Among them, only overflowing springs show good quality, due to the presence of impermeable rocks isolating groundwater from the sea. Good-quality springs represent about 28% of the total karst water drained to the Adriatic and Ionian Seas, and about 83% of this high-quality water drain in the northernmost sector of the studied area, along a 1.5 km-long coastal strip. The strong increase in population, particularly in the summer-season due tourism, as well as construction of new urban areas, represent the main sources of likely pollution for some of the good-quality springs. The high anthropic pressure on groundwater resources has three main effects at this study area: worsening of seawater intrusion, reduction of freshwater availability at specific areas, and contribution to spring salinization [Eftimi et al., 2023].

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Geochemical Background Values and Spatial Distribution of Major and Trace elements in unpolluted soils of Sicilian Region (Italy)

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The objectives of this study are to evaluate, for the topsoils of Sicily region (Italy), the geochemical background values of major and trace elements, considered potentially toxic to human health, and to establish the relationship between soil chemicals and the local geology by multivariate statistical procedures. 83 samples from the topsoil (0-0.2 m) were collected in several sites far away from potential anthropogenic pollution sources. Total concentrations of potentially toxic elements were extracted via acid digestion and quantified via inductively coupled plasma (ICP-MS/ICP-OES). The results revealed: pH values fall within a range from moderately acidic (5.9) to neutral (7.2); low levels of organic matter and highly heterogeneous mineralogical characteristics. The major elements Ca, Fe and Al (Ca: 26300.0 ppm; Fe: 23300.0 ppm; Al: 19400.0 ppm), the trace elements Zn and V (Zn: 68.8 ppm; V: 40.0 ppm), showed the highest median concentrations in the study, while the major elements Mn, Sr and Ba (Mn: 320.0 ppm; Sr: 111.0 ppm; Ba: 77.5 ppm), and the trace elements Bi e Ag (Bi: 0.2 ppm; Ag: 0.1 ppm), presented the lowest levels. Several methods have been employed to determine the value of geochemical background ($Me \pm 2MAD$; Boxplot; Iterative 2σ ; Grouping of data with 60% coefficient of variation; 90° - 95° - 99° ; $AvA \pm 2\sigma$; PROUcl software). Among the results obtained, methods $Me \pm 2MAD$, 95° and PROUcl, have proven to be the most suitable for the dataset. The spatial distribution of elements has been calculated by stochastic simulations on a convex-concave boundary at a resolution of 10 km. The use of this geostatistical technique allows the local uncertainty of the estimated content values to be known. The results of this study contribute to the creation of an environmental database of soils in the Sicilian region and will serve as the basis for future studies.

Compound-Specific Stable Isotope Analysis (CSIA) to assess Bioremediation of Chlorinated Hydrocarbons in Groundwater: Integration with Biomolecular Tools in a Long-Term Monitoring

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Compound-Specific Isotope Analysis (CSIA) has emerged as a state-of-the-art technique in contaminant hydrology to trace and differentiate pollution sources and to monitor and quantify active in-situ biodegradation reactions in both engineered and natural attenuation remediation settings. Systematic microbially-induced changes in isotope signatures of organic contaminants (isotope fractionation) provide direct evidence of biotransformation, allowing estimation of in situ degradation rates and evaluation of groundwater bioremediation performance and pathways. The presented study documents a case of extensive field application of CSIA to assess Enhanced Natural Attenuation (ENA) at a large, chlorohydrocarbons-contaminated site in Southern Italy. Stable carbon isotope analysis (¹³C-CSIA) of chlorinated ethanes and ethenes has been performed every six months for over three years at distinct modules and sub-areas within the site, each characterized by different baseline conditions, prevailing contaminants, and amendments applied for biostimulation, covering all stages of the remediation project (pilot test, pre- and post-operation monitoring). The collection of a large dataset of isotopic signatures and its integration with biomolecular data in a multi-proxy approach, enabled both the identification and quantification of ongoing relevant (bio)degradative processes, as well as distinguishing rebound effects. Results offered advanced technical-scientific consultancy to site managers and regulatory bodies, ultimately fostering informed decision-making in the remediation of a complex, heterogeneous site.

Geochemical Characterization and Distribution of Potentially Toxic Elements in Stream Sediments: Insights from the Former Mercury Mining District of Mt. Amiata, Central Italy

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From 1860 to 1980, when all Hg mines definitively shut down, more than 100,000 t of liquid Hg were produced from the world-class Mt. Amiata mining area. The eastern sector of Mt. Amiata hosts 8 of the most important Hg mines from where cinnabar was cultivated (e.g., Abbadia San Salvatore, Pietrineri, Morone, Solforate, and Siele). Several streams and creeks drain these sites and contribute to enrich the concentration of potentially toxic elements (PTEs, e.g., Cr, Ni, Co, V, Hg, As and Sb) of those rivers they flow into (e.g. Orcia and Paglia). Here, seventy-five stream sediments were collected and analyzed for mineralogical (XRD) and chemical (XRF and ICP-MS) investigations. Stream sediment geochemistry is mostly used in geochemical exploration as it represents a powerful tool for detecting the presence of ore deposits. Stream sediments are also helpful in geological field mapping and soil erosion studies. In this work, we applied an environmentally-oriented approach, since we aimed at geochemically investigating the effects on the stream sediments due to the mining activity affecting this area for more than one century. After the mineralogical and geochemical characterization of the stream sediments, two distinct groups were recognized. The first one refers to the erosion of the Mt. Amiata volcanic products, while the second one belongs to the sedimentary realm that is largely found at the foothills of the volcanic complex. While Hg and As are enriched in the central-northern area, corresponding to either the former mining areas or not-exploited hydrothermalized zones, Sb results to be preferentially enriched in the southernmost portion. The streams draining the sedimentary cover exhibit relatively high concentrations of V, Cr, and Co. Our data allow to determine the PTE geochemical baseline levels along this roughly N-S oriented strip where most mining activity was concentrated since they can provide a strong basis for environmental legislation.

Geochemical Baseline values of PTEs in soils in the eastern portion of Mt. Amiata (Tuscany, Italy)

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Establishing the geochemical background or geochemical baseline (GB) values in natural environments is of paramount importance for both soil management and identification whether the concentrations of Potentially Toxic Elements (PTEs) may be originated by natural sources and processes (e.g., rock weathering, presence of mineralization, climatic processes, or morphology) or human activities, such as vehicular traffic, industries, agrozootechnical practices, and so forth. GBs are of pivotal importance in mineralized areas such as that of the Mt. Amiata region (Tuscany, central Italy), where Hg mines have been exploited since the Etruscan period until the 1980s. In this study, an area of 120 km², covering the eastern portion of the Mt. Amiata volcano, was considered to define the GB values in soils of selected PTEs (i.e., Hg, As, Sb, Cr, Ni, V, Co, and Cu). Consequently, 163 soils (top-soil: 10-50 cm, and sub-soil: 50-150 cm), mostly developed on a volcanic (mainly trachyte) and sedimentary (clay-limestone, clay-sandy, and jasper soils) substrate were sampled throughout the study area using a hybrid sampling grid: i) a rectangular one (1×2 km) covering the entire area under examination, and ii) a smaller square one (1×1 km) near the main mining/mineralized areas. Regardless of substrate, the concentrations of Hg, As, Sb, Cr, Co, Ni, Cu, and V were highly variable and up to 1030, 367, 301, 925, 54, 937, 120, and 187 mg/kg, and up to 1250, 309, 985, 1024, 74, 158, 105, and 218 mg/kg for the top- and sub-soils, respectively. Owing to the significant differences highlighted among the four geological domains, the four datasets were considered separately to define the geochemical baseline value for each PTE. The statistical approach evidenced that Hg, As, Cr, Co, V, and sometimes Sb were characterized by much higher values than those imposed by the Italian law. These data are useful for regional and local authorities when small-to-big infrastructures are to be built.

MUSE: a computational tool to support spatio-temporal uncertainty evaluation in Geochemistry

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Assessing the heterogeneity of a regionalized variable is a challenging problem in real applications, where a quantitative approach is needed. Numerical modelling of transport and reaction of species in solution requires the knowledge of the geometry of geological bodies permeated by waters. Geological structures' complexity, due to physical processes such as deposition and deformation, may be difficult to discern. Data collected in *in-situ* surveys provides only sparse and partial knowledge of the domain.

Our research aims to increase knowledge of geological settings by assessing uncertainty in environmental data. Uncertainty quantification comes from a stochastic approach based on geometric supports (structured/unstructured meshes), embedding the (continuous and categorical) variable distribution and enabling the recognition of permeable bodies featured by pinch-out or erosional structures. The method works efficiently for application in concave-convex computational domains spanning two or three dimensions, and it can be generalized for *Natural Systems* by treating environmental data as regionalized variables.

The methodology is embedded in MUSE, a stochastic-based tool for Modeling Uncertainty as a Support for Environment [Miola et al., 2022]. It is designed and implemented as a modular tool, incorporating geometry processing techniques to handle the morphology of survey domains, geostatistics to estimate spatial dependence laws (automatically and/or supervised), and stochastic approaches to evaluate estimates and uncertainty.

Remarkable outcomes demonstrate the effectiveness and adaptability of MUSE application, even in complex geological structures (e.g., deformed bodies) where locally varying anisotropy conditions may appear. By applying stratigraphic coordinates transformation, the spatial continuity is accurately preserved in the domain. MUSE tool is still ongoing and further tests are planned to assess its efficacy and computational capabilities.

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Geochemistry of a not really inert production residue (KEU)

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KEU (Kraftanlagen Energie und Umwelttechnik) is a by-product of a pyrolyzed waste of sewage sludge produced by wastewater treatment of leather. This material is indeed processed after inertization, being mixed with construction and demolition materials, to obtain a sintering granulate. The “inertization” by thermal treatment is questionable as well as the source of the “original material” mixed with KEU. The resulting material poses environmental issues in addition to those already present in the KEU since it was used as roadbed in several areas of Tuscany (central Italy). To have an evaluation of the environmental impact of KEU, different leaching tests were carried out. The 1-day leachates resulted to be enriched in many heavy metals with concentrations, in most cases, up to hundreds to thousands of µg/L. Despite a general decrease in the 7-days leachates, high contents of some heavy metals were still recorded. Our study indicates that the CO₂-saturated MilliQ water is able to remove more heavy metals than MilliQ water and that the inertization process presently used to stabilize unwanted toxic elements is not efficient and its use as by-product is strongly discouraged. Another issue is related to the presence of tens of µg/L of CrVI in the leaching tests. The rainwater-KEU material interaction processes can indeed transfer unwanted elements to water bodies (rivers and aquifers), spoiling the quality of the blue resource. Consequently, more efficient inertization processes to treat the pristine mud waste are to be improved and correctly tested. The KEU-rich products should geochemically be characterized since, as in this case, relatively high contents of critical and strategic metals were determined (e.g. REE, W, Mo, Ta, Nb) and an economic assessment about their possible exploitation should be provided.

Where does humidity come from? Moisture uptake analysis and stable isotope composition of single precipitation events (northern Tuscany)

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The moisture source and rainout history of air masses are important climatic controls on the stable isotope signature of precipitation [Lachniet, 2009]. The ongoing climate change has among its main consequences the alteration of the water cycle, which includes changes in the seasonal distribution and amount of precipitation, rainfall regime, and atmospheric disturbance systems. Hence, understanding the relationship between moisture origin and stable isotopes in precipitation is essential to obtain a clearer climatic and hydrological perspective allowing for the proper management of vulnerable resources to climate change, especially in the Mediterranean. Isotopic datasets with high frequency sampling are more suitable than cumulative monthly samples for understanding the influence of atmospheric processes on the isotopic signal of precipitation. Here we present the results of an event-based isotopic survey coupled with a Lagrangian moisture diagnostic in a catchment of the western Mediterranean (northern Tuscany). 34 single precipitation events were collected from March 2020 to June 2021 at two different altitudes (4.5 and 660 m a.s.l.) and analyzed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Moisture uptake analysis was performed on 5-day back-trajectories initialized for each rainy hour for each event, and moisture uptake regions were identified. Most of the moisture (75%) came from marine areas, especially from the western Mediterranean (38%), North Atlantic Ocean (19%) and eastern Mediterranean (9%). Continental moisture accounted for less than 25% (Iberian Peninsula, North Africa, France, and UK). Recycled continental vapor increased from winter to spring and summer. This trend partly reflects the large inter-event isotopic variability, which is better explained by the combined influence of air temperature, precipitation amount, and moisture uptake regions.

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Groundwater and legacy mining: stable isotopes of dissolved sulfates as a marker of contamination sources

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Carbonate aquifers represent an essential source of water supply worldwide, despite their high vulnerability to contamination and short-term climatic fluctuations. Multidisciplinary surveys coupling isotope geochemistry and hydrochemistry allow us to unravel solutes origin and processes affecting the water resource quality. Such an approach steers the optimal management of complex aquifers, which is essential for their sustainable exploitation and protection from contaminants. This work addresses the critical issues tied to the coexistence of abandoned mines and valuable groundwater hosted within carbonate aquifers in a past-mining district of the Apuan Alps (Italy). Some springs are threatened by acid mine drainages and contaminated stream from potentially toxic elements (e.g., Tl, As, Sb) [Doveri et al. 2021]. Water samples were collected from a mine drainage, the stream, and springs in the 2016-2018 period. Stable isotopes ($\delta^{18}\text{O}$ - $\delta^2\text{H}$ - H_2O , $\delta^{18}\text{O}$ - $\delta^{34}\text{S}$ - SO_4), major and trace elements were analyzed. Pyrite and Fe-Al-K secondary sulfates were also analyzed for sulfur isotopes. The sulfate isotopes, along with chemical data, revealed different groundwater flow systems and multiple sources of sulfates and sulfate-related elements. The $\delta^{18}\text{O}$ - SO_4 and $\delta^{34}\text{S}$ - SO_4 ranged from a minimum of 0.7‰ and -9.6‰ to a maximum of 10.6‰ and 14.9‰, respectively. Mine drainage, stream, and two springs exhibited lower isotope values of sulfate, indicating sulfide oxidation, associated with higher Tl contents. Conversely, one Tl-free spring showed higher $\delta^{18}\text{O}$ - $\delta^{34}\text{S}$ - SO_4 values, typical of evaporitic dissolution. This indicates a deeper and longer groundwater flow feeding this spring, which seems to be isolated and protected from contamination.

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Biochar as a sustainable amendment to mitigate mercury mobility at the sediment-water interface: evidences from incubation experiments using benthic chambers

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Mercury (Hg) contaminated sediments may act as a secondary source of contamination, especially during anoxic events that occur naturally in shallow, semi-confined aquatic systems such as fish farms. Indeed, anoxia and high organic matter (OM) production may promote the release of Hg species into the water column, thus posing a risk to marine life and human health. In this context, sorbent amendments may represent an economical and ecologically sustainable approach to mitigate Hg mobility and its availability to be methylated [Gilmour et al., 2013, 2018]. This study aims at evaluating the ability of biochar from vineyard pruning residues in reducing Hg mobility at the sediment-water interface (SWI) in one of the most productive fish farms of the Marano and Grado Lagoon, affected by Hg contamination [Covelli et al., 2012].

Laboratory incubation experiments were conducted using two benthic chambers to compare biochar-amended and untreated sediments. Temporal changes in dissolved Hg, dissolved oxygen (DO), redox potential, Fe, Mn, H₂S, N-NO₃⁻, N-NO₂⁻, N-NH₄⁺, and P-PO₄³⁻ were monitored for 35 days. At early stage, a faster DO consumption and more reductive conditions were observed, especially in the untreated system, as well as an increase in dissolved N-NH₄⁺, P-PO₄³⁻, Fe and Mn, as a result of intense OM mineralisation processes and reductive dissolution of oxy-hydroxides, respectively. Once anoxia was reached, the control system showed the highest Hg concentrations (46.7 ± 11.1 ng/L) whereas notably lower concentrations were observed in the biochar-amended chamber (12.7 ± 3.8 ng/L). After re-oxygenation, oxic conditions were rapidly restored in the amended system with respect to the control chamber where anoxia and elevated Hg concentrations (37.2 ± 11.5 ng/L) lasted for a further 6 days. The results suggest that biochar is effective in reducing Hg mobility at the SWI, limiting the development of anoxic conditions and promoting re-oxygenation.

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Thermal coats and changing environmental conditions affect indoor/outdoor radon exchange dynamics and indoor radon levels

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The renovation of existing building stock in terms of improving their insulation, has become increasingly urgent in recent years to cut CO₂ emissions. Reducing loss of energy across the building envelope makes edifices more airtight, enhancing indoor pollutants accumulation, unless further steps are taken to test for and mitigate indoor pollutants, such as radon gas. Radon is the leading cause of lung cancer in non-smokers. It can seep into indoor spaces through small cracks and openings where the building contacts the ground or through emission from building material.

The role of thermal coats applied to the exterior of a building on radon gas exchange was simulated and studied using a scale model room made of a volcanic rock rich in radon precursors. The effect of wind and outdoor pressure on radon diffusion through the coats was simulated and monitored over time showing that equilibrium radon concentration is modified due to changing pressure and concentration gradients between the scarcely permeable coat and the outdoor. This survey was carried out with waterproof materials applied to the internal walls of the room, thus reducing the influx of radon.

The presence of thick, partially permeable insulation layers placed on the outside of the walls delays radon diffusion outwards, responding to any external actions contrasting this flow. During the week the laboratory ventilation reduce indoor radon in the external coat, removing the high concentration layer at the interface with the room and favouring an outward air flow. Conversely, the absence of laboratory ventilation during the weekends produces the high concentration layer at the room/coat interface. Thus, radon is retained in the coat leading to an increase of indoor radon. The temperature is not a controlling factor in these experiments because it was constant over time.

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Perfluorinated and perfluoroalkyl substances (PFAS) in groundwater and surface water in Turin Metropolitan Area (Italy)

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Perfluorinated and perfluoroalkyl substances (PFASs) are synthetic, toxic, polluting and astoundingly recalcitrant molecules. Arpa Piemonte has been monitoring a total of 19 different PFASs in freshwater in the Piedmont region since 2021. Here, PFAS data from shallow (72) and deep (55) wells, 28 sites along selected streams and 1 lake in the Turin Metropolitan Area collected in the 2021-2023 period are discussed. The aims are to investigate the occurrence of PFASs in freshwater, estimate the PFAS load in streams and examine the contribution of potential point PFAS source categories (i.e., contaminated and reclaimed sites, industries, landfills and wastewater treatment plants).

PFASs, varying in composition with water samples with no clear spatial and temporal trend, are revealed in 44 and 31% of the investigated shallow and deep wells in a total concentration (Σ PFASs) of 0.01-0.71 and 0.01-0.16 $\mu\text{g/L}$, respectively. No direct correlation between the Σ PFASs values nor the detection PFAS rates with the number of individual PFAS point sources located at the upgradient position of the sampling sites of shallow wells is observed, implying both the existence of additional contamination sources and an unpredictable diffusion of these chemicals in the water.

PFASs are found in 93% of the sampling points in streams with Σ PFASs values of 0.0002-0.3222 $\mu\text{g/L}$, whilst they do not occur in the investigated lake. The composition and concentration of PFASs in streams vary with time and sampling sites, likely because of seasonal changes in the characteristics and compositions of wastewater treatment plants' effluents. The annual Σ PFASs loads in the Po River, where all the other streams join, downstream Turin Metropolitan Area were about 200-350 kg/y.

Since some PFAS concentrations exceeded the thresholds set by Italy and the EU guidelines, efforts must be spent to monitor PFASs at the level of potential sources of contamination: i.e., industrial effluents and manufacturing processes.

Effect of energy efficiency measures on indoor radon with the model room approach

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Thermal renovation of existing homes is a highly effective method for short term reduction of CO₂ emissions. As such, retrofitting the existing building stock has become more pressing and state grants and subsidies have been promoted all over the world. Unfortunately, energy saving measure are boosting the concept of a strongly insulated building envelope to avoid dispersion and air exchange between inside and outside. New high performing insulation layers are all addressed to increase the thermal behaviour of the building envelope. On the other hand, this approach strongly increases the risk of concentration of indoor domestic and natural pollutants, such as radon, a very dangerous agent which is considered the second cause of lung cancer after smoke.

The effect of energy efficiency measures on indoor radon is here investigated with the scale model room approach. The scale model room was built with a very porous ignimbrite with high radon exhalation rates and was previously used to test waterproof materials applied on the inner walls of the chamber as radon barrier, with and without room ventilation (Portaro et al., 2023). In this study the influence of two insulation materials (mineral wool and extruded polystyrene), characterized by different thermal conductivity and porosity was evaluated. Eight-centimeter thick insulation coatings were placed over the outdoor walls of the model room according to various settings: with and without inner barriers, with and without room ventilation at different rates. Equilibrium radon activity concentrations were monitored and compared to assess the effect of mineral wool and extruded polystyrene on the increase of radon levels. The two coats reduce air exchange with the outside leading to a significant increase in indoor radon levels, especially when waterproof materials are not applied to the inner walls of the room and no pressurization is active. Extruded polystyrene enhances these effects compared to the more permeable mineral wool.

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Critical Raw Materials (CRMs) investigation in dismissed historical Volcanogenic Massive Sulfide (VMS) deposits in the Northern Apennine (Italy)

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Northern Italy has more than 100 abandoned mining sites, most of which are now under investigation to determine their Critical Raw Materials (CRMs, *i.e.*, minerals or elements whose supply is not enough to satisfy the global demand) content [Kiss et al., 2023]. Dismissed mining sites in the Emilia Romagna region are no exception, in particular, the Boccassuolo mines, related to ophiolitic terrains (Boccassuolo Ophiolite). These sites are receiving new interest due to the various disseminated historical extractive spots of Cyprus-type Volcanogenic Massive Sulfide deposits [Garuti et al., 2011]. These deposits, also known as VMS, occur here as pods within small bodies of ophiolitic basalts cropping out as olistoliths in the Northern Apennine External Ligurian units and owe their origin to metal-rich hydrothermal fluid circulation which developed quartz-sulfide veins when mixed with seawater through a fissures network [Saccani, 2015]. They are characterized by sequences of pillow lavas associated with serpentine and gabbro breccias, radiolarian cherts, limestones, and abundant serpentinized subcontinental mantle peridotites [Kiss et al., 2023]. In this area, basalts show OCTZ chemical features with transitional-MORB affinity and a garnet signature ($Dy_n/Yb_0=1.2-1.4$). Bulk rock geochemical analyses for major and trace elements were performed, and preliminary results agree with previous studies [*e.g.*, Barrie & Hannington, 1999, Zaccarini & Garuti, 2008]: these deposits are Cu and Cu-Zn VMS types, with almost no Pb (<1 ppm), with Cu max. 200*UCC, Zn max. 118*UCC, and Ag max. 12*UCC [Rudnick & Gao, 2014]. Such preliminary data provide the first relevant information to map trace metal enrichment distribution in the main rocks. Radiogenic (Sr-Nd-Pb) and stable (S-C) isotopic analyses and another sampling in Montecreto and other sites in the Emilia Romagna region are planned to compare the results, increase the available database, and estimate the CRMs volumes.

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Hydrogeological and geochemical study of surface groundwater and baseline values in the Nuraxi Figus area (SW Sardinia)

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As part of the project on the determination of baseline values (VF) in abandoned mining areas, entrusted by the Region of Sardinia to ARPAS, the Agency signed a collaboration agreement with Carbosulcis SpA for the determination of the background values of the groundwater surface in the Nuraxi Figus site in the SW of Sardinia. The Agency performed the survey in collaboration with the University of Cagliari Departments, and Carbosulcis, the company managing the closure and remediation of the coal mine.

The investigations started from the request to determine the VFs of the surficial aquifer, were extended to the different groundwater issues allowing a more general understanding of the hydrogeology of the area with the aim of proposing operational suggestions to be managed in the ongoing activities of mine reclamation. Direct recharge of the aquifer was calculated and preliminary groundwater dating was carried out using tritium decay times. These studies, together with observations of data collected by Carbosulcis in the past and new surveys and sampling performed, allowed to be refined the conceptual model (MC) and to provide a clear picture of the hydrogeological context of the area. This MC encompasses three aquifers distinct in elevation, circulation, and hydrogeochemical composition: shallow in Quaternary deposits, deep in Tertiary volcanites, and the deepest in Eocene sediments where is located the Coal deposits. The MC and estimated VFs on the surface aquifer were assumed by a specific determination of the Competent Authority, the Italian Ministry of Environment and Energy Security as a base for the prescriptions regarding the mine reclamation.

As a result of investigations carried out, it seems clear the essential role of building a robust Conceptual Model that can drive the choices related not only to the determination of baseline geochemical values, but also to the monitoring and control of the environmental impact of the reclamation work in a closing mine area.

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Degradation index for landfill gas species to quantify the biodegradation efficiency of novel landfill biocover soils

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Landfills release significant amount of landfill gases (LFGs) into the atmosphere through diffuse emissions from topsoil. LFG mainly consists of CH₄, CO₂, and a minor fraction of non-methane volatile organic compounds (VOCs). Methane is one of the major greenhouse gases, while several VOCs concur to air pollution and severe risk to human health. Efforts to minimize LFG diffuse emissions generally converge to the application of cover soils (LCSs) on deposited waste, acting as biofilter for LFG. The LFG biodegradation efficiency of LCSs is related to several physicochemical factors favoring the formation of aerobic microbial consortia as methanotrophs capable of oxidizing CH₄ to CO₂, and VOCs-degrading bacteria. The present study aims to investigate methods for the improvement of the potential LCSs biodegradation efficiency, based on a laboratory experiment simulating a landfill environment. The degradation processes affecting each LFG compound passing through a common LCS are compared to those occurring in three novel LCSs, created by treating natural soil with sewage sludge and landfill leachate. An index *I*, describing the behavior of each LFG species, is calculated by dividing its concentration in gases from the LCSs by the concentration in biogas from a chamber containing the degrading organic matter feeding the LFG. Accordingly, the value of the *I* index of each LFG species is inversely proportional to its degradation, providing a direct estimation of the LCS efficiency. The test showed that gases from treated soils, especially that treated with only sewage sludge, have *I* values for most LFG species, including those typically recalcitrant to biodegradation, significantly lower than those of gases from the untreated soil, providing useful indication for treatment applications of soils at landfill scale.

SESSION 3 - GEOCHEMISTRY IN VOLCANIC, GEOTHERMAL AND SEISMIC AREAS

Conveners:

Alessandra Correale (INGV, Sezione di Palermo), Anna Gioncada (DST, Università di Pisa),
Andrea Ricci (INGV, Sezione di Palermo)



Figure caption: Caldara di Manziana (Central Italy). Photo by Lisa Ricci

“Nyiragongo, The Forbidden Volcano”. Ten years of geochemical investigation

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Mt. Nyiragongo is an active stratovolcano located in the Democratic Republic of Congo, within the Virunga National Park on the western side of the African Rift Valley. Nyiragongo is known worldwide for the spectacular molten lava lake inside its main crater, which has always fascinated scientists and tourists. At the same time, it also has the reputation of being one of the most dangerous volcanoes in the world as it is located about 18 km from the city of Goma, now inhabited by about one million people who are exposed to the risks associated with volcanic activity. Nyiragongo was referred to as ‘*the forbidden volcano*’ by Haroun Tazieff in 1975, both because of the logistical difficulty of reaching and studying the lava lake and its emissions, and because of the dramatic social and geopolitical situation in which the Kivu region is historically tormented by continuous wars. Since 2011, I had the opportunity and fortune to study Nyiragongo and the nearby Nyamulagira volcano. The last expedition took place during the recent eruption (22 May 2021). Over the past ten years, numerous collaborations with local researchers have been established, which continue to this day despite enormous logistic difficulties. The research topics we have focused on are the study of the gases and particles emitted by the volcanic plume and the resulting impact on atmospheric deposition. Moreover, the study of rainfall chemistry has highlighted the risks to which the population living on the downwind side of the volcano is exposed, with serious consequences on people’s health. In particular, the 2021 eruption emphasised the high vulnerability of the population, but it also made possible to involve citizens in the collection of data during the seismic swarm, to map the fractures that opened in the city, and to identify anomalous degassing areas. A good example of best practice and citizen science for volcanic monitoring.

Characterization of CO₂ and CH₄ diffuse degassing from Furnas Lake hydrothermal area, São Miguel Island (Azores, Portugal)

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Furnas volcano in São Miguel Island is the most significant degassing area in the Azores archipelago, releasing large amounts of CO₂ through fumaroles and diffuse soil degassing (> 1000 t d⁻¹).

In volcanological research, quantification of CO₂ volcanic-hydrothermal fraction is typically pursued for monitoring purposes and to estimate the Earth's carbon budget.

The goal of the present investigation is to complement the typical data of CO₂ diffuse degassing from soil with those of CH₄, a compound that is usually overlooked in the hydrothermal environment despite having a heavy potential impact on the environment being a strong greenhouse gas.

A soil CO₂ degassing survey performed in the Furnas Lake fumarolic field with the accumulation chamber was coupled with the collection of gases from the accumulation chamber at each site of flux measurement for the detection of the gas fluxes and the identification of carbon sources. The gaseous samples were analyzed to determine CO₂ and CH₄ concentrations and their $\delta^{13}\text{C}$ values.

The isotopic analysis allowed to provide insights into secondary processes affecting the hydrothermal gases flowing through the soil and to better recognize the possible contribution of gases from microbial activity.

Coupling isotopic and compositional data allowed to identify the gas source of the "intermediate" populations resulting from the statistical analysis based on CO₂ flux values, leading to a more accurate estimate of volcanic-hydrothermal vs. biogenic CO₂ output. In particular, the CO₂ biogenic threshold for the present work was set at 50 g m⁻² d⁻¹.

Gases released through diffuse emission had a CH₄/CO₂ ratio over 40 times higher than that typical of fumarolic discharges in Furnas. This indicates that CH₄ from the soil has a twofold origin, hydrothermal and biogenic, the latter being the dominant source in the study area as also supported by the $\delta^{13}\text{C}$ values of this gas.

Statistical techniques for the evaluation of heat and carbon fluxes: application to Larderello-Travale geothermal region

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The Larderello – Travale geothermal system is located in the central part of the Tuscany region (Italy). It is a large-scale steam-dominated system with reservoir temperatures that can exceed 350°C [Bellani et al., 2004]. The characteristic high heat flow in this particular area is due to the presence of a thermal anomaly caused by the intrusion of a large Pliocene batholith into the upper crust [Musumeci et al., 2002]. This work aims at analyzing data of diffuse degassing and the relationships between carbon emissions and heat fluxes at the surface. In particular, we are interested in analyzing the distribution of CO₂ and CH₄ emissions and soil temperatures in the Monterotondo Marittimo and Sasso Pisano areas. To achieve our goal we will apply different statistical techniques that include well-known Graphical Statistical Approaches [e.g., Sinclair, 1974; Chiodini et. al., 1998] and modern methods based on a computational approach. Also, we aim at developing a Python library to allow replicating our findings and entitle an easy application of the proposed methods to other study cases.

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Mapping of the gas manifestations at Pantelleria island (Italy) through classical geochemical methods and Unmanned Aircraft Systems: Preliminary results from PANTA REI project

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In the framework of the INGV project Pianeta Dinamico (PANTAREI), all known gas manifestations have been resampled, while during the same campaigns many other have been located thanks to the indications from colleagues involved in the geological mapping of the island and from local inhabitants. All manifestations have been located through a handheld GPS receiver and their coordinates will be uploaded in a GIS project. Temperature measurements were taken at 15 and 50 cm depth. Gas samples were taken inserting a tube at 50 cm depth and their chemical compositions were analysed at INGV-Pa.

The collected gas samples can be included into two main groups. The first shows temperatures between 70 °C and boiling and the chemical composition is CO₂-dominated with abundant H₂ and CH₄. The second group shows temperatures mostly <60°C and the chemical composition is air-dominated with CO₂ mostly <10 %, absence of H₂ and low CH₄.

The first group can be interpreted as fed by the deep high enthalpy geothermal system through the main deep tectonic or volcano-tectonic structures. The second group is mainly found in the area of the NW flank of Mt. Grande and its manifestations are possibly fed only by the perched low enthalpy hydrothermal aquifer.

Due to the fact that a large part of the island is very difficult to access, we took advantage from reconnaissance flights with UAS carrying thermal IR cameras to locate thermal anomalies and with multispectral cameras to discover areas in which the vegetation is affected by geogenic degassing.

The first UAS surveys were made on the south flank of Mt. Grande where large areas with stunted or absent vegetation strongly contrasting with the nearby areas covered by rich vegetation. Such areas are very difficult to reach on foot because of the intricate vegetation. The survey showed many thermal anomalies evidencing an active degassing of geothermal fluids in these areas that will be the target of gas sampling and direct temperature measurements.

The Deep Mercury Cycle: an updated database of natural sources against anthropogenic emissions

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The Earth's mantle is the major reservoir of volatiles such as C and S that, in the form of CO₂ and SO₂ are the major carriers of mercury (Hg) to the atmosphere [Edwards et al., 2021]. A preliminary database built up from literature data allows us to draw a global Hg cycle [Yin et al. 2024]; however, there are no available data to constrain the Deep Mercury Cycle (DMC).

The aim of this study is to constrain the origin and the end of the DMC through an updated database that combines Hg fluxes from volcanic and seismic areas, along with currently available Hg concentrations in natural rocks.

The majority of mantle and crustal rocks are Hg depleted (up to 68 ppb and 47 ppb, respectively) [Yin et al., 2024] with respect to sedimentary rocks (up to 36750 ppb) [Grasby et al., 2019; Yin et al., 2024] testifying the role of magma degassing and the Hg precipitation from gaseous phases that represents among the main mechanisms of Hg enrichment in sedimentary rocks. The high volatility of mantle-derived Hg is also highlighted by the few data available on Hg volcanic emissions ranging from 0.01 ton·yr⁻¹ to over 350 ton·yr⁻¹ [Edwards et al., 2021]. However, recently remote sensing techniques has allowed to estimate a possible global budget of Hg volcanic emissions (232 ton·yr⁻¹) [Geyman et al., 2023].

An updated Hg database of natural emissions will be presented, and the results discussed in comparison with the known anthropogenic Hg production.

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Fluid-rock interaction: the carbon dioxide (CO₂) origin camouflage

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In geochemical studies, CO₂ is used as a pivotal tracer to investigate the gas origin and processes occurring during their transfer to the surface. This application also enables the verification of the movement and interaction of crustal and mantle fluids within Earth lithospheric framework. However, the highly reactive nature of this chemical species can result in ambiguous fingerprints that are very difficult to decipher. In Buttitta et al. (2023) the ¹³C/¹²C fractionation of CO₂ following rock-CO₂ interaction, CO₂ dissolution in water and degassing/precipitation process are discussed to figure out the relationship between deep processes and characteristic of shallow fluid, by considering the nature of the deep reservoirs and the 3-D structure of the crust. Now, we focused to CO₂-rock interaction considering the main mineral phases in crustal layers (calcite, dolomite, aragonite, graphite and siderite) at different temperature (T), pressure (P) and V_{CO₂}/V_{mineral} (ϕ) conditions. The preliminary results show that a large variation in δ¹³C values of original CO₂ isotopic signature occurs depending on conditions: at low P and T the δ¹³C-CO_{2(gas)} data tend toward more negative values (up to -7‰ unity for, CO₂-Calcite), conversely at high T, P and lower ϕ conditions the isotopic values tend toward more positive (up to +9‰ unity for, CO₂-Calcite). In conclusion, the CO₂-minerals interaction within the Earth crust can lead to substantial and complex changes in the carbon isotopic composition CO₂. This is heavily dependent on environmental conditions such as temperature and pressure that can mask the pristine carbon isotopic signature. This study shows how CO₂-rocks interaction processes may modify the isotopic signature of original CO₂ across different geological conditions. This could improve interpretations of signals on the surface and make reconstructions about gas origin and processes occurring more accurate.

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The hydrothermal system of Lipari Island (Aeolian Islands, southern Italy): towards an estimation of the geothermal potential

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The estimation of geothermal potential for evaluating the feasibility of exploitation of low, medium, and high enthalpy geothermal resources is an essential step in a scenario of global climate change that necessarily leads to a transition addressed to renewable resources for a sustainable energy production. This is even more relevant in those areas where the geothermal potential would allow energy autonomy, such as the small islands of the Aeolian archipelago (southern Italy), which are currently dependent on fossil fuels. This topic is one of the main issues of the IRGIE Project, aimed at providing an inventory of the geothermal resources of the Aeolian Islands by investigating the geochemical features of fluid manifestations (i.e. thermal waters and gas emissions). In this study, the preliminary results of a geochemical survey carried out at Lipari Island, where gas and water samples were collected for chemical and isotopic analyses, are presented. Sampling sites included the main fumarolized area (Cava di Caolino), the San Calogero hot spring, and 9 wells from the eastern side of the island. The Cava di Caolino fumarole (~ 90 °C) is CO₂-rich, with CH₄, N₂ and H₂S up to 0.93, 0.75 and 0.06 %, respectively, and with R/Ra of 4.3. The 10 water samples, displaying temperature and TDS values ranging from 22.7 to 48 °C and from 731 to 45,038 mg/L, respectively, show different compositions: Na-Cl, Na-SO₄, Na-(HCO₃, SO₄), (Ca, Mg)-SO₄, (Ca, Mg, Na)-SO₄ and Ca-(Cl, SO₄). Such a wide geochemical variability is likely produced by multiple and overlapping geochemical processes, such as water-rock interaction, seawater contribution, input of CO₂-rich fluids and steam heated shallow water bodies characterized by H₂S oxidation. New surveys on the north and western portions of the island are planned shortly to complete the geochemical investigation of the island and to develop a conceptual geothermal circulation model, also integrated with geophysical data.

A new geochemical characterization of the main fluid emissions in the Friuli Venezia Giulia Region to investigate the geothermal potential of low-to-medium enthalpy systems: preliminary results

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The growing interest in research and exploitation of low-to-medium geothermal resources promoted by INGV to develop a scientific program aimed at investigating the geochemical features of natural fluid manifestations in different areas of Italy. In the framework of the EMOTION project (GeochemICAL characterization of fluid manifestations in central-northern Italy for geothermal assessment and development of the geothermal fluid natIOnal web portal) focusing on the investigation of thermal and mineral fluid discharges in central-northern Italy, a survey for the collection of fluids discharged from the main natural springs in the Friuli Venezia Giulia (FVG) Region was carried out by UNIFI geochemical team in March 2024. The aim of the study is to consolidate and implement the geochemical database available in bibliography with an exhaustive set of chemical and isotopic analyses to better characterize and understand the regional thermal resource. Up to 16 waters with temperatures ranging between 6.3 and 39 °C, conductivity ranging between 83 and 20,500 $\mu\text{S}/\text{cm}$ were sampled to determine major anion and cation components, trace elements, water isotopes, $\delta^{34}\text{S}-\text{SO}_4$ and $\delta^{13}\text{C}-\text{TDIC}$. The composition of dissolved gases and the $\delta^{13}\text{C}-\text{CO}_2$ and $\delta^{13}\text{C}-\text{CH}_4$ values were also determined. Three types of waters were recognized: 1) shallow aquifers, characterized by low salinity and temperature (i.e. up to 11.5 °C and 577 $\mu\text{S}/\text{cm}$, respectively), dominated by a $\text{Ca}(\text{Mg})-\text{HCO}_3$ facies; 2) hot water showing high temperature and salinity (i.e. 39.4 °C and 20,500 $\mu\text{S}/\text{cm}$, respectively) and a $\text{Na}-\text{Cl}-\text{Br}$ composition; 3) $\text{Ca}(\text{Mg})-\text{SO}_4$ and Fe-rich waters, characterized by low temperature and medium-high salinity (i.e. up to 11.5 °C and 1600 $\mu\text{S}/\text{cm}$ respectively). The latter were likely related to water-rock interaction with geological formations rich in gypsum and sulphate minerals. Upcoming analyses of the planned extensive parameterization will provide more details on the circulation systems that feed these sources.

Geochemical characterization and monitoring of groundwater in seismically active areas in southern Apennine (Italy): the study of Matese and Pollino areas

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In the framework of the FURTHER INGV Departmental Project, aimed at investigating the role of fluids in the preparatory phase of earthquakes in the southern Apennines through a multidisciplinary approach, the geochemical monitoring of groundwater from carbonate aquifers is ongoing since 2020 in the Matese and Pollino areas, located in two seismically active sectors of the Apennines belt. While in the Matese system the occurrence of deeply derived CO₂ degassing was already recognized [Di Luccio et al., 2022 and ref. therein] for the Pollino a comprehensive geochemical database was not available yet. At Matese, four high flow rate springs characterized by different amounts of dissolved deep CO₂ have been seasonally monitored, while at Pollino, a general survey of both thermal and large flow rate springs was carried out in order to both characterize the groundwater and to produce a complete chemical-isotopic dataset. In the latter area, six springs, both cold and thermal, were selected for the seasonal monitoring. Geochemical investigation has been aimed at recognizing the presence of deep CO₂, at quantifying its flux by applying a dissolved-carbon mass-balance, and at characterizing the time variability of the different carbon sources. At Pollino, the carbon dissolved in the cold groundwaters results from water-rock interaction and biological sources, while a possible deep-carbon contribution cannot be excluded for Latronico and Sibarite thermal waters. At Matese the seasonal variability of the different carbon contributions was characterized, representing an important reference monitoring puposed. Discrete, low-frequency, geochemical data have been integrated with high-frequency data (temperature, electrical conductivity and water level) acquired by multi-parametric probes at Grassano spring (Matese) and Sibarite well (Pollino). These sites resulted suitable for hosting geochemical stations as a part of the emerging INGV national hydrogeochemical network.

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Noble gases (He, Ne, Ar) as tracers of metasomatized Subcontinental Lithospheric Mantle: an example from the Ivrea-Verbano Zone

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Noble gases are sensitive tracers of mantle heterogeneity and provide important insights into the evolution of the subcontinental lithospheric mantle (SCLM). However, the pristine He signature of the SCLM [6.1 ± 2.1 Ra, Day et al., 2015] can be modified by several processes such as the fluxing of metasomatizing melts or fluids [e.g., Matsumoto et al., 2005]. Furthermore, rock samples from SCLM often show complex histories of metamorphism, deformation, and fluid interaction, and, in this way, noble gases data can help to determine possible crust-mantle interactions [Hilton and Porcelli, 2014].

We performed noble gases analyses on samples from the Ivrea-Verbano Zone (Southern Italian Alps), a well-known lower continental crust to upper mantle sequence exposed in northwest Italy [Decarlis et al., 2023]. In detail, we analyzed six representative rocks (three mantle peridotites, two intrusive gabbroid rocks, and one metamorphic granulite) from the main outcropping lithological units in the studied area, in order to investigate the noble gases signature of the different domains (deep crust and upper mantle). Isotope $^3\text{He}/^4\text{He}$ ratios in mantle peridotite range between 0.08 and 0.42 Ra, and they are significantly more radiogenic than mantle-derived samples. Gabbro and granulite samples show $^3\text{He}/^4\text{He}$ ratios of 0.15-0.19 Ra and 0.25 Ra respectively. Interestingly, Ne isotope ratios in mantle peridotite ($^{20}\text{Ne}/^{22}\text{Ne} = 9.57\text{-}10.26$, $^{21}\text{Ne}/^{22}\text{Ne} = 0.03\text{-}10.26$) show a mixing trend between the air and the radiogenic component expected in the crustal composition, while the gabbro and granulite samples plot near the air component. As regards the Ar isotope ratios, all samples appear rich in radiogenic component ($^{40}\text{Ar}/^{36}\text{Ar}$ up to 2980).

Our preliminary results show how a highly radiogenic crust-like noble gases signature can be preserved in lithospheric mantle domains, possible metasomatized by past subduction-related processes.

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Exploring the influence of seismic events on water hydrochemistry: preliminary results from the Mt. Conero area (central Italy) following the 5.5 Mw Marche offshore earthquake on November 9, 2022

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The occurrence of seismic events may induce changes, referred as seismic tracers, in the hydrogeochemistry of the fluids circulating in the surroundings of the epicentral area. The identification of seismic tracers aimed at earthquake forecast is one of the major targets in the current research. In this work, we report the preliminary results from a pre- and post-seismic water monitoring carried out in the Mt. Conero area (central Italy) after the 5.5 Mw Marche offshore earthquake (Lat. 43.9830, Long. 13.4240, depth 5 km) on November 9, 2022. The monitoring included three piezometers, i.e., Montacuto (MAC), Vallemiano (VAL) and Betelico (BET), located at different distances (45-55 km) from the epicentre and with depths comprised between 15 and 30 m. All waters were collected within 48 hrs from the mainshock and periodically for one year after the event. The water geochemistry of BET site was available from May to October 2022, i.e., five months before the earthquake. The aim was to evaluate the influence of the event on the water hydrogeochemistry. MAC and VAL did not show any relevant change. Contrarily, significant variations were displayed by BET. Its geochemical facies, characterized by a calcium-bicarbonate and a TDS (Total Dissolved Solids) <1000 mg/L, typical of shallow aquifers, indeed became sodium-chloride with TDS >3500 mg/L, since the end of June 2022, i.e., four months before the mainshock. About a week after the main event, the water chemistry returned to be Ca-HCO₃ and no changes were detected during the monitoring year. Minor to major variations were also recorded in trace element contents (i.e., B, Mn, Zn). The origin of these changes is likely represented by a mixing process between the shallow aquifers (Ca-HCO₃) and deep-sourced Na-Cl waters, likely favored by the earthquake preparation processes. The reported variations are among the most impressive geochemical evidences ever detected before a seismic event or ever reported in the literature.

Forty years of geochemical data at Solfatara, Campi Flegrei

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The systematic sampling of the main fumaroles of Solfatara (Campi Flegrei, Italy) started during the bradyseismic crisis of 1983-84. In the late 1990s, diffusive CO₂ emissions measurements also became part of the monitoring activity through systematic campaigns. In these 40 years of investigations almost unique databases were created including thousands of chemical and isotopic analyses of fumaroles and hundreds estimations of the diffuse CO₂ emission. These databases provided the base of numerous geochemical and interdisciplinary scientific works to understand the processes occurring in the hydrothermal-magmatic system of Campi Flegrei, a caldera in unrest since 2005. The main results obtained by this effort indicate the pivotal role of magma degassing in the current crisis of Campi Flegrei. The deep magmatic fluids are injected into the hydrothermal system during episodes of magma degassing. These injections cause pressurization and heating of the hydrothermal systems, earthquakes, ground deformations, changes in fumarole compositions and escalating CO₂ emission at the surface. The expulsion of these fluids constitutes the most energetic process currently occurring at Campi Flegrei; it is, in fact, more energetic than ground deformation and seismic activity. In this work, we present a review of these different aspects and new data concerning a recent S anomaly of the main fumaroles.

Preliminary results of the investigation of the main feeding areas at the Larderello geothermal system, focus on the Le Biancane area

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The Larderello geothermal system, situated in the southern part of Tuscany, is being used for electricity production since the beginning of the last century. With the ongoing activity, during the '70s the wells started to reach deeper horizons and in some of them the reinjection of waste fluids has been introduced. The latter process led to the formation of a liquid plume which modified the isotopic composition of the pristine fluid present at depth.

During the following years research has been conducted to see how the reinjection was affecting the isotopic composition and gas/steam ratio of the well discharges [Calore et al., 1982; D'Amore et al., 1987], as well as regarding the potential recharge areas [Ceccarelli et al., 1987]. However, after those years no further studies have been carried out. Nowadays, the Larderello geothermal system lacks a detailed study of the potential feeding areas and there is no updated dataset with the springs and hydraulic regime of the Larderello area, especially considering the variations in the last decades due to the ongoing climate change.

Here we aim to investigate the location of the main feeding zones of this system, with a focus on the Le Biancane area. This area is situated in the southern part of the geothermal field and is characterized by the outcrop of the shallower reservoir. To obtain the local isotopic marker we sampled springs on a wide area, selecting those at the base of small reliefs, with local circulation, which could be useful for an isotope hydrological approach. The samples have been analysed for chemical and isotopic composition (dD, d18O), and Tritium content. Unfortunately, around the Le Biancane, few perennial springs were found, and we therefore installed five rain gauges, to directly sample the rainwater. Finally, these isotopic data are compared to fumaroles and well discharges that are present at the Le Biancane.

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The 2021-22 unrest of La Fossa volcano (Vulcano Island, Aeolian Archipelago) by the side of fumarole chemistry: clues on the magmatic source in the prodromal and ongoing phases

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La Fossa volcano (Vulcano Island, Italy), since its last eruption (1888-90), remains in a quiescence state interrupted by phases of unrest. These episodes were always marked by an increase in the vapour output, generally paired by an increase in local seismicity. During the volcano awakening, the composition of the fumarolic vapour, which is interpreted as the result of a mixing process between magmatic and hydrothermal fluids, responds to the increased input of magmatic volatiles, overwhelming the background contribution of hydrothermal H₂O-rich vapour. Other than being a marker of the relative contribution of magmatic and hydrothermal fluids, the fumarole composition can reveal some clues on the magmatic or hydrothermal sources of fluids, which can be differently involved over time. It has been speculated that some of the observed unrest phases, like in 2004-05, would have involved only the shallowest ponding zone of a latitic reservoir [Paonita et al., 2013]. Other unrest phases, like the period 1988-93, would have been triggered by fluids coming from the deepest parts of the reservoir. The involvement of the deepest, more primitive magma reservoirs or, instead, the shallowest ones has crucial implications in terms of the amount of fluids entering the volcano-hydrothermal system, potentially able to induce pressurization and disrupt its equilibrium.

In this paper, we present the data on chemical and isotopic composition of the vapour collected in the high temperature fumaroles in the period 2011- 2023, encompassing the last unrest episode, which started in September 2021. We discuss an original dataset along with previously published data, to provide a comprehensive interpretative framework of the sources of fluids feeding the crater fumaroles over time. The presented data reveal that the 2021 unrest was heralded by a 3-years long preparatory phase. The breakthrough of the 2021 unrest stimulated different gas or magma reservoirs, whose contribution was never noticed in the past. We tentatively provide some insights on the nature and location of these new magmatic sources.

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High frequency $\delta^{13}\text{C}_{\text{CO}_2}$ measurements in soil gas from Mt. Etna: preliminary results of the IMPACT project

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IMPACT is an INGV-funded project, mainly aimed at deciphering which are the main factors controlling magmatic unrest, and how fast magma ascent is within the crust, which is the behaviour and timing of changing some parameters in the phases preceding a magmatic eruption on Mt. Etna. In this framework, we investigated the behaviour of CO_2 in soil gas. Continuous measurements of the diffuse flux from soils through monitoring networks could provide useful signals to assess magma dynamics and to evaluate the state of volcanic activity (Etna, Vulcano, Stromboli, Pitòn de La Fumaise etc etc) (Liuzzo et al., 2013). However, CO_2 emitted from the soil is the result of mixing between different sources, such as the atmosphere, biosphere, and inorganic processes. Each source has a distinct and partially overlapping carbon isotopic signature, and the contribution of each source could be quantified by determining the carbon isotopic composition of CO_2 . For this purpose, since 2021, a Thermo Delta Ray – IRIS has been installed in the field to collect unprecedented, up to 1 Hz, $\delta^{13}\text{C}_{\text{CO}_2}$ data in soil gas emissions from two sites located along the N and the E flank of the Mt Etna respectively. The choice of these sites was driven by several factors: they are located in proximity to local tectonic discontinuities which enhance the migration of deep gases through the soil, the concentration of the gas in the soil was in the measurement range ($\text{CO}_2 = 400\text{-}3500$ ppm) of the instrument, electricity, and Internet access, as well as a shelter where the instrument could be safely installed. The gas was collected from a 2 m long metal probe inserted into the soil to minimize shallow atmospheric perturbation. Measurements were performed according to a previously described protocol [Boudoire et al., 2020]. Here, we present the first results recorded at both sites.

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Origin and Geochemistry of Fluid Manifestations in the Ukrainian Carpathians: A Comprehensive Review and Novel Interpretations

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Carbon or CO₂ degassing from the Earth's crust is a result of two distinct sources: a "point-source" contribution emanating from active volcanoes through plumes and volcanic-hydrothermal areas, and a more widespread "diffuse" input from tectonically active regions. While the deeply derived CO₂ from tectonically active zones remains a subject of quantification, it is increasingly recognized as a significant contributor to Earth's CO₂ degassing. Various studies have underscored that CO₂ from these tectonically active regions dissolves into groundwater circulating within extensive regional aquifers, predominantly hosted by permeable formations within active orogens. The Eastern Carpathians Volcanic Range (ECVR) encompasses a vast chronological spectrum, spanning from millions to tens of thousands of years. Despite the absence of recent volcanic activity, the ECVR is renowned as one of Eastern Europe's foremost regions for CO₂ volcanic degassing. While ongoing studies are shedding light on the Romanian segment of the Eastern Carpathians, the Ukrainian counterpart remains largely unexplored. Although some fluid geochemical studies were conducted in the 1970s and 1980s, interpretations regarding the origins of these fluids were deficient. To elucidate the fluid manifestations in the Ukrainian Carpathians, an extensive database comprising over 1000 water samples and more than 290 gas samples was meticulously compiled. Drawing upon this comprehensive dataset, a thorough review was undertaken to discern the origin and geochemistry of the fluids, leading to innovative interpretations aimed at: i) quantifying the carbon flux through the principal groundwater systems; ii) estimating subsurface reservoir temperatures; iii) evaluating the extent to which volcanic carbon, as a diffuse source, is influenced by the tectonic framework; and iv) generating a regional degassing map alongside a conceptual model for the Ukrainian Eastern Carpathians.

Geogenic degassing from the tectonic area of North Macedonia

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Several studies are devoted to quantify the geogenic carbon release from the Earth's interior and its impact on the global carbon cycle, with much emphasis placed on active tectonic areas. Balkan Peninsula is characterized by Cenozoic volcanic systems, regional active fault systems, intense seismicity, and positive geothermal anomalies. These features favour the occurrence of geothermal areas, cold CO₂-rich springs, and diffuse soil degassing. North Macedonia belongs to the Southern Balkan Peninsula and presents many gas manifestations, but their characterization is until now scarce. This study represents the first catalogue, although probably still incomplete, about such manifestations in North Macedonia. From their chemistry three groups of gas emissions were identified: (i) N₂-dominated, (ii) CO₂-dominated, and (iii) H₂S-rich, located in the eastern, central and western parts of Macedonia, respectively. The three geographically well separated groups are, mainly, related to major active tectonic structures and to Cenozoic volcanism. Highest CO₂ values are found along major fault systems, suggesting a geogenic source of gases. The isotopic composition of carbon dioxide ($\delta^{13}\text{C}_{\text{CO}_2} = -15.7 - +1.0 \text{ ‰}$ vs. V-PDB) and helium ($\text{R/R}_A = 0.1 - 1.8$), together with the high CO₂/³He ratio, suggest a dominantly crustal origin (mainly from limestones), with small mantle contributions (up to 20%). Finally, the H₂S might be related to thermochemical sulfate reduction process (TSR) occurring in evaporite deposits, which are present in the stratigraphic record.

Are we able to listen what the fumarolic fluids of the Solfatara have been telling us for about 40 years?

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Recently, we reviewed the geoscientific information on the Solfatara magmatic-hydrothermal system and elaborated new gas geothermometers and geobarometers, properly calibrated for possible depressurization paths of Solfatara fluids, also taking into account deviations from ideality [Marini et al., 2022].

On September 2023, we submitted to JVGR a paper in which we revised the conceptual model of the Solfatara magmatic-hydrothermal system, based on our geothermometric and geobarometric results, also considering the most recent data [Buono et al. 2023], as well as the information from other geosciences. Given the importance of the topic, we decided to anticipate here the main results of our work, which could also be of interest to decision makers in the management of the ongoing crisis, waiting for the JVGR reviewers to complete their work.

Our revised conceptual model includes:

- (i) a shallow reservoir (0.25-0.45 km depth), in which CO equilibrates
- (ii) an intermediate reservoir (2.7-4 km depth), in which CH₄ equilibrates
- (iii) a deep reservoir (6.5-7.5 km depth), in which H₂S equilibrates.

In the time interval 1983-2022, the temperature and total fluid pressure of the shallow reservoir remained close to 220°C and 25 bar, whereas noteworthy, gradual increases in temperature and total fluid pressure took place in the intermediate and deep reservoirs, with peak values of 590-620 °C and 1200-1400 bar in the intermediate reservoir and 1010-1040°C and 3000-3200 bar in the deep reservoir, in 2020. Accepting that the bradyseism is governed by the pressurization-depressurization of the intermediate reservoir, changes in temperature and total fluid pressure of the intermediate reservoir are of utmost interest to understand local ground movements. The total fluid pressure in the deep reservoir appears to act as “on-off switch” of magmatic degassing. We also used the revised conceptual model to predict possible future scenarios in the lack of external factors.

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The effects of elemental sulfur precipitation/dissolution in low-temperature geothermal systems: refined H₂-H₂S-H₂O gas indicators with application to La Soufrière de Guadeloupe (Lesser Antilles)

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Hydrogen sulfide (H₂S) is the major sulfur-bearing gas species released in low-temperature fumarolic environments and elemental sulfur is formed through the oxidation of H₂S via sublimation. In this process of oxidation, H₂S reacts with oxygen in the air in presence of water (H₂O) and produces widespread halos of S₈ which appears as yellow crystals around the fumarole. Liquid elemental sulfur can sometimes be discharged from fumaroles, where it appears as a bright yellow or orange flow) out of the fumarole, pushed by pressure buildup during thermal peaks of the hydrothermal activity. The discharge of liquid elemental sulfur from fumaroles is not a common occurrence and can provide valuable insights into the geochemical forcing factors acting on a boiling hydrothermal liquid at depth. A thermodynamic parameterization of sulfur discharge in fumarolic environment is then highly needed to move on quantitative grounds and establish whether the hydrothermal regime behind the variations in elemental sulfur emissions reflects purely internal hydrothermal factors or deep magma-related solicitations (injection of S-rich fluids). Nevertheless, the phase diagram of sulfur is surely the most complex one among those of all chemical elements. This is because of the many molecular and crystallographic forms that sulfur has. From a practical standpoint, this results in large uncertainties of S-bearing species other than H₂S.

Here, we refine the thermodynamic parameterization of the formation of elemental sulfur, including for which conditions liquid sulfur may form in fumarolic conduits of volcanic systems. The resulting parameterization is tested for La Soufrière de Guadeloupe, where liquid sulfur projections have been detected.

Mercury in shallow silicic magma reservoirs: Lessons from Valle Mosso Pluton (Western Alps, Italy)

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The amount of mercury (Hg) released by active volcanoes into the atmosphere is genetically linked to the underlying magmatic plumbing systems. Nonetheless, our understanding of the cycling of this highly volatile trace metal within any subvolcanic magmatic systems remains limited because the distribution and concentration of Hg in minerals and magmas before degassing are still unconstrained. To this goal, we aimed to investigate Hg in the upper crustal Valle Mosso pluton (VMP) of the transcrustal Sesia Magmatic System (SMS) (Western Alps, Italy), which is an exemplary “fossil” magma chamber that fueled eruptions in the early Permian. From bottom to top, the VMP exposes 1) sulfide-bearing quartz-monzonite cumulates, 2) homogeneous monzogranitic crystal mush, and 3) high-silica granites bearing miarolitic cavities. We used in-situ synchrotron X-ray fluorescence mapping at the XRF beamline (Elettra, Trieste) on selected areas of thin sections of these granites to locate Hg in minerals in which it could be partitioned (sulfides, quartz, biotite, amphiboles, feldspars *s.l.*, oxides and apatites) and Cold-Vapour-Atomic-Fluorescence-Spectroscopy (CV-AFS) for whole rock Hg analyses. XRF mapping identified other chalcophiles (e.g., S, Cu, Zn, As, Ge, and Ga) than Hg, suggesting that minerals host very low concentrations of Hg (< µg/g). CV-AFS shows similar Hg concentrations among each VMP unit, from 0.63 to 4.3 ng/g. However, because Hg does not correlate against SiO₂, other mechanisms than magma differentiation control the Hg cycle in VMP. As suggested by the presence of miarolitic cavities in high-silica granites, the percolation of volatiles through the VMP could be a viable mechanism. Further petrographic work aimed at recognizing this mechanism in mineral textures and new whole-rock analyses on the volatile trace metals identified via XRF mapping will place more constraints on the cycle of Hg and other metals in a granitic system.

Geochemical and isotopic investigations of thermo - and mineral waters: Republic of Moldova

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The aim of this study was to describe the geochemical and isotopic features of the main thermo- and mineral waters from the Republic of Moldova (RM) to trace their flow pathways and evaluate the presence of deep fluid sources. RM has an area of 33,840 km² and lies within the East European Precambrian Platform. The deep aquifers occur at a relatively shallow depth in the northern part and up to 200–1,000 m depth in the southern sector and hosted within the Vendian (Ediacarian) and crystalline basement rocks, Silurian crystalline limestone, Cretaceous limestone, Baden-Sarmatian limestone and clay-sand deposits, middle Sarmatian limestone and clay-sand layers. More than 50 water were collected and analyzed. They had temperature up to 28 °C, neutral to alkaline pH, Total Dissolved Solids between 515 and 75,846 mg/L and Eh values mostly negative. They displayed a relatively high compositional variability, as they belong to Ca(Mg)-HCO₃(SO₄), Na-Cl and Na-HCO₃ facies. In the mineralized waters from the Baden-Sarmatian aquifer, the trace element distribution revealed high contents of F⁻, I⁻ and Br⁻ (up to 13, 24 and 141 mg/L, respectively). High As and Ni values were found in the Dubasari waters (up to 13.8 and 43 μg/L, respectively). Dissolved gases were mainly dominated by N₂ (from 0.16 to 0.78 mmol/L), while CO₂ and CH₄ ranged from 0.02 to 0.66 mmol/L and from 0.00005 to 0.44 mmol/L, respectively. The δ¹⁸O and δ²H values were ranging from -15.8 to -0.9 ‰ and from -104.5 to -32.8 ‰ vs. V-SMOW, respectively, suggesting a meteoric source slightly modified by prolonged water-rock interactions. The δ¹³C-CO₂ values were from -25.2 to +2.8 ‰ vs. PDB, the most positive ones being associated with the waters collected from the oil field in the southernmost part of the country. The absence of free gases and the secondary geochemical processes that affect the RM thermomineral waters, a reliable estimate of the thermal equilibrium temperature of the reservoirs is presently unlikely.

Numerical modelling of the volcanic plume composition: applications to estimate the chemistry of the volcanic outgassing compared to field measurements

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The study and the interpretation of the volcanic outgassing is central to analyse the composition of the degassed plume and its interaction with the atmospheric air. In this research, we use a multidisciplinary approach combining numerical modelling and data from field measurements to analyse the outgassing at open vent volcanoes, where we can observe the volatiles release directly from the bubbles within the melt to the atmosphere. Specifically, we focus on the degassing of the Nyiragongo lava lake (Democratic Republic of Congo) which represents a perfect case study for the opportunity to take measurements on the gas composition soon after the release from the melt. Our main goal is to simulate the volatiles transition from the melt to the atmosphere and their chemical evolution after the release from the volcano. To do this, we use different steps of simulations starting with the selection of the possible initial volatile composition dissolved in the melt and within the bubbles. At this point, we simulate the gas chemical speciation at the equilibrium [French, 1966; Holloway, 1981; Fegley, 2013; Gaillard and Scaillet, 2014; Schaefer and Fegley, 2017; Ortenzi et al., 2020] immediately after the release of the volatiles from the bubbles to the atmosphere. After that, when the volcanic gases start to mix with the cold and oxidised surrounding atmosphere we observe a further volatile chemical speciation due to the change from an equilibrium to a chemical kinetics system [Kuhn et al., 2022]. At this stage, we model the evolution of the gas chemical composition during the first seconds of the mixing between the atmospheric air and the volcanic gas phases [Roberts et al., 2019; Kuhn et al., 2022; Goodwin et al., 2023]. During the presentation we will show simulations of volcanic plume compositions in the COHS system highlighting both the effect of the thermodynamic equilibrium and the chemical kinetics and compare them with observational data from the literature.

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The Irpinia Groundwater Monitoring Network in the frame of the Myburp Project: first results from cold and thermal waters in a seismically active sector of southern Apennines (Campania region, Italy)

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Irpinia is located in one of the most seismic-prone sector of southern Apennines; many strong earthquakes, up to $M = 7$, took place in the region in the last centuries [Rovida et al., 2022]. Seismicity is due to the presence of large, NW-SE striking, regional normal fault systems and is mainly confined in the uppermost 15 km of the crust [e.g. De Matteis et al., 2012].

Regional faults and associated fracture networks act as preferential pathways for deep-seated fluids, allowing both the presence of thermal Spas and a CO_2 diffuse degassing from waters and soils. By contrast, the shallow cold groundwater circulation is due to the infiltration of meteoric water into the large carbonate karst aquifers, which represent the primary sources of drinking water of the Campania region and surroundings. Thermal and cold waters have different physical-chemical features, show a wide chemical and isotopic composition thus reflecting various degrees of gas-water-rock interaction processes, distinct underground hydrological circuits and infiltration depths. Based on the above-reported considerations, Irpinia can be considered as an ideal test site where deepening the relationships among faults, earthquakes and fluid geochemistry.

As such, between September 2023 and February 2024 a continuous monitoring network was set up. Four CTD-Divers were installed in springs and wells not affected by anthropic disturbances: San Teodoro thermal well, Ofanto and Gavitoni cold springs and Cantani hypothermal spring. The probes take measurements of water temperature, electrical conductivity and level/pressure every 5 minutes. The main goals of the monitoring are to: i) detect possible seasonal trends in the monitored parameters, ii) investigate timing and shape of aquifers response to both rainfall and snowfall to study their underground dynamics and iii) deepen the interplay between fluids and earthquakes.

Characteristic of the monitored sites are discussed and preliminary time series are showed.

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IRGIE – Inventory of the Geothermal Resources of Aeolian Islands

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IRGIE is a three-year (2023-2026) national geothermal project that aspires to facilitate energy autonomy for small islands like the Aeolian archipelago. These islands currently depend predominantly on diesel generators, which represent a non-sustainable environmental and economic option. The primary idea is to support the integration of a wider array of renewable energy sources, including photovoltaic, solar, wind and geothermal. Although geothermal energy has traditionally occupied a marginal position in global energy scenarios, it can play a significant role at the local level, satisfying energy demands extensively. In this framework, IRGIE aims to identify and characterise the geothermal resources within the Aeolian Islands. This includes an assessment of the theoretical geothermal potential and the formulation of recommendations for appropriate technologies to harness low-, medium-, and high-temperature geothermal resources based on the local energy demands. To achieve these goals, and to characterise the geothermal fluid and estimate the temperature, pressure, and volume of the geothermal reservoir, geophysical and geochemical surveys are underway on the archipelago. Furthermore, geochemical numerical models of flow and reactive transport will be developed for one or more promising sites. This will enhance understanding of the pre-, sin-, and post-exploitation states of the geothermal system. Another key element of the IRGIE project is its focus on outreach and educational initiatives. The project assesses the current level of social acceptance of geothermal energy among the local population and aims to enhance awareness and knowledge about geothermal energy among both young people and adults within the Aeolian Islands.

IRGIE is coordinated by INGV and funded by Regione Siciliana. The research team comprises universities, research institutions, and specialists in geothermal energy, thereby demonstrating a synergical and multidisciplinary approach.

The Emotion Project: towards a national web portal of geothermal fluids

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Investigating the chemical and physical properties of hydrothermal fluid discharges (thermal springs, gas-rich waters and gas vents) is essential for characterizing geothermal resources. A free access web portal making easily available detailed geochemical data of geothermal fluids can represent a powerful tool for supporting geothermal exploration and promoting the exploitation of geothermal resources. However, data portals for fully accessible thermal, mineral and gas-rich water compositions are currently limited and need to be improved at both national and international levels, limiting also data sharing and reuse, a key point of Open Science and the FAIR data principles (Findable, Accessible, Interoperable, and Reusable).

The three-year-long EMOTION Project aims to fill this gap by developing a public data portal for the geothermal manifestations in central-northern Italy, gathering together bibliographic data, frequently dispersed and of not easy-access, with those from new dedicated geochemical surveys. The Project also aspires to propose a data and meta-data structure and formats for thermal and gas-rich spring geochemical datasets.

The proposed portal is designed to be solid, consistent, user-friendly and interactive and is constructed according to the following steps: 1) deep literature review of available geochemical data; 2) standardization of the geochemical and geographic parameters; 3) data curation; 4) data analysis for identifying areas not exhaustively covered by previous studies; 5) integration with new data produced by EMOTION; 6) data management into a central database; 7) making data available through free download and visualization by interactive maps and selected geochemical graphs.

The EMOTION data portal, fostering the data availability, holds the potential to contribute to the development of use of the geothermal resources, inspiring the scientific community and the stakeholders for further research and projects.

Active degassing of crustal CO₂ in areas of tectonic collision: A case study from the Pollino and Calabria sectors (Southern Italy)

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The current increase of the CO₂ in atmosphere, and its link with the global climate change, provides a strong motivation to understand the natural processes that control geological carbon cycling. The release of natural CO₂ from the Earth's interior into the atmosphere mainly occur through both volcanic and non-volcanic sources in a variety of tectonic settings. A quantitative understanding of CO₂ outgassing is thus critical for decoding the link between the global carbon budget, the different natural processes (e.g., volcanic eruption and earthquake nucleation) and the effects on the climate evolution over geological time. On a global scale, is known that CO₂ emission in atmosphere is associated with tectonically/seismically active zones [Chiodini et al., 2004; Tamburello et al., 2018], in fact numerous studies in the last decades emphasized the important contribution of these areas to the Earth carbon budget [e.g., Minissale, 2004; Italiano et al., 2008; Caracausi and Sulli, 2019; Frondini et al., 2019; Chiodini et al., 2020; Groppo et al., 2022]. Here, we report the results of a geochemical survey in a continental area far from volcanism aimed at quantifying CO₂ emissions through cold and thermal springs of two seismically active areas in the southern Italy (Pollino Massif and Calabrian arc in Southern Italy). The chemical and isotopic (He and C) composition of fluids allowed to identify two different domains: a shallow system dominated by gas components of atmospheric and biogenic origin, and a deeper system in which crustal/deep fluids (CO₂ and He) are dominant. The He isotopic composition (R/Ra) range from 0.03 to 1.1 Ra revealing a variable atmospheric contamination that mix with crustal derived He. The mantle He components is lower than 3%. Combining He and C isotope data, we also explored the possible secondary processes (gas dissolution and mineral precipitation) that act to modify the chemistry of pristine volatiles. We figure out that gas dissolution in the groundwater strongly affect the amount of the dissolved gases and correcting for this process, we estimated a deep C output in the studied areas from 2.3×10^7 to 6.1×10^8 mol year⁻¹. These values correspond to deep CO₂ fluxes comparable with those estimated in several active and inactive volcanic areas and in continental regions affected by metamorphic CO₂ degassing (e.g., the southern margin of the Tibetan Plateau).

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Origin and geological controls on the geochemistry of hydrocarbons released by intense CO₂ degassing in seismically active areas of Central Italy

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Seismically active post-orogenic extensional areas are frequently characterized by intense CO₂ degassing. As suggested by several studies on the Apennines such CO₂-rich fluids play an important role in faulting processes and possibly even in earthquake triggering. In order to study the preparatory phase of earthquakes and the role of fluids along the Apennines, the INGV (National Institute of Geophysics and Volcanology) has been working on the development and deployment in the field of a dense network of modern seismic, geodetic, geochemical, and geophysical sensors. In this framework, understanding the sources of fluids and the processes controlling their chemical and isotopic composition during storage in crustal reservoirs and transfer to the surface is crucial to improve our ability to correctly interpret multiparametric time series. Along with CO₂, smaller, yet significant amounts of light hydrocarbons are emitted. Their origin and applicability in seismo-geochemical monitoring networks are still unclear. Here, we present chemical and isotopic data for hydrocarbons discharged from CO₂-dominated gas emissions located in seismically active areas of Central Italy. Geochemical evidences strongly indicate that hydrocarbons are predominantly derived from cracking of organic matter, possibly hosted in Mesozoic carbonate rocks. We show that CH₄/(C₂H₆+C₃H₈), δ¹³C-CH₄, carbon isotopic pattern of C₁-C₄ hydrocarbons and helium isotopic composition are correlated and vary with the distance of gas emissions from high heat flux areas. We suggest that differences in thermal history and hydrogeological conditions of the crust at the hydrocarbon formation depth may be responsible for such variability. Hydrocarbons might therefore contribute in unravelling the sources of fluids circulating in the crust and the processes that control their geochemical characteristics and could provide new clues to understand the response of fluids to crustal processes in seismic areas.

Alkaline lakes as natural CO₂ sinks: the case study of Bogoria lake (Kenya)

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Alkaline (or soda) lakes are extreme aqueous systems characterized by high salinities, pH values higher than 9, sodium as the main cation and high contents of bicarbonates and carbonates [Pecoraino et al. 2015]. Key factors that favor the formation of alkaline lakes are arid/semi-arid climates (high evaporation rate, low water inflow), and structural/geological settings that enhance the development of closed basins and limit the water outflow [Pecoraino et al. 2015]. Alkaline lakes frequently occur in areas of strong natural CO₂ degassing (i.e. the East African Rift, EAR). In order to assess the impact of alkaline lakes on the dynamic of the degassing process, the geochemistry of the Bogoria lake system (Eastern branch of EAR) has been investigated based on data provided by Cioni et al. [1992]. Bogoria lake is a soda lake with a drainage basin of 705 km², mainly fed by thermo-mineral springs associated to a geothermal system with reservoir temperature of 163-170°C and partial pressure of CO₂ between 10 and 20 bar [Cioni et al., 1992]. The total amount of CO₂ transported by Bogoria springwaters, computed by means on the Total Dissolved Inorganic Carbon and the spring flow rates, is 1.39×10^9 mol/yr. At discharging condition, Bogoria springs are oversaturated with calcite and dolomite but undersaturated with respect to alkaline carbonates (e.g. natron, trona, gaylussite). This suggests that a large amount of CO₂ is fixed in the solid phase as Ca-Mg carbonates, according to the precipitation sequence of Hardie and Eugster [1970] and Eugster and Jones [1979]. As a consequence, the deeply-derived CO₂ flux that enters the Bogoria hydrothermal system is orders of magnitude higher than the CO₂ flux from the hydrothermal system to the atmosphere. Bogoria lake behaves as a natural sink for CO₂, suggesting that alkalines lakes deserve further studies as natural analogues of CO₂ sequestration through mineral precipitation.

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Monitoring fumarole emissions on the flanks of Mount Etna and correlation with volcanic activity

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Etna's activity over the last ten years has been characterized by intense explosive activity with numerous lava fountains. In order to test new monitoring parameters for monitoring volcanic activity at Mt. Etna, a geochemical station for the measurement of soil CO₂ concentrations was first installed in 2019 for one month into a vent formed in 2002 along the North-East rift, at altitude of 2450 m asl. The 2002 vent was chosen because inside it there are some steam fumaroles characterized by large gas emissions both of CO₂ and of CH₄. In 2019 it was observed that shortly before a strong explosive episode on 8 September at the NE summit crater there was a decrease in measured CO₂ concentrations that could not be attributed to changes in environmental factors (mostly wind speed and barometric pressure). In that occasion, the observed fluctuations could be related with the fast dynamics of magmatic fluids into Etna's conduits. In the following years we had the opportunity to test and better evaluate that preliminary hypothesis, as numerous paroxysmal episodes occurred on Etna. It is noteworthy that during the first two years of the station operation, until about mid-July 2021, CO₂ anomalies (mostly in terms of strong and short-lived negative peaks) were systematically followed after about 24-48 hours by increases in volcanic activity in the summit craters (Strombolian activity at Northeast Crater in 2019 and Strombolian activity at Southeast Crater in 2020) or by more intense eruptive events (as in the case of the 2021 cycle of paroxysms at the Southeast crater). From this point of view, negative CO₂ anomalies are interpreted as due to sudden movements of gas-rich magma from a reservoir located between 1 and 6 km below sea level towards a shallow reservoir located between 1 and 2 km above sea level.

Exploring the geothermal potential of the Alpehue Hydrothermal Field (Sollipulli volcano, Southern Chile) through gas geothermometry, soil CO₂ degassing, and superficial heat release

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Achieving carbon neutrality by the next few decades requires exploring clean energy alternatives, including geothermal energy sources. Despite Chile's strategic geodynamic setting and abundant volcanic activity, geothermal energy sources in the country have still been poorly exploited. The Alpehue Hydrothermal Field (AHF), located near the Sollipulli Volcano in the Southern Volcanic Zone, shows promise as a significant geothermal resource. A comprehensive geothermal exploration survey was conducted, including evaluating the chemical composition of hydrothermal gases, geothermometric calculations, and soil CO₂ flux and temperature measurements. Our findings indicate that the hydrothermal gases released at the AHF exhibit a dominant mantle origin with little crustal and ASW contribution, showing He isotopic composition among the highest reported in the SVZ of Chile, with Rc/Ra values ranging between 7.3 and 7.9. The $\delta^{13}\text{C-CO}_2$ display a mixed origin between a mantle source and, to a lesser extent, crustal sediments, consistent with other SVZ volcanic systems. A deep geothermal reservoir showing temperatures between 235 and 270 °C calculated using gas geothermometers in the H₂/Ar* vs. CO₂/Ar* and CO/CO₂ vs. CH₄/CO₂ systems feeds these gases.

Concerning soil CO₂ fluxes, two different populations were identified corresponding to the background emission related to the soil biological activity (mean $\sim 7.7 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) and the endogenous source related to the AHF reservoir (mean $\sim 461 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$). The calculated heat flow rate, based on empirical equations derived from soil temperature measurements, of the AHF is approximately 3.3 Mw with a total heat flux of 156 thermal Mw·km⁻², which could be considered a medium geothermal potential comparable to other systems worldwide. Although further studies are needed to address its exploitability fully, this study presents favourable characteristics of the AHF that make it a promising avenue for further exploration.

Study of groundwater and superficial water in tectonically active regions: quantification of deep CO₂ emissions and geochemical monitoring of seismic activity

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Central Italy's geological features, such as active faults, earthquakes, CO₂-degassing anomalies, and large groundwater circulation, create an ideal setting for Earth Sciences research. The process of deep CO₂ degassing leads to CO₂-rich groundwater and feedback mechanisms between CO₂ anomalies and seismic activity were highlighted: significant variations in dissolved deep CO₂ were associated with large Apennine earthquakes [Chiodini et al., 2020]. This study presents the results of a two-year geochemical campaign conducted in the Tiber river basin (TRB) to investigate the relationship between deeply-derived CO₂ and seismicity, and the transfer of carbon from the deep interior to the atmosphere. The TRB receives deep CO₂-rich groundwaters from large springs some of which are known to be sensitive to earthquakes. The sampled river waters exhibit compositions and variability similar to those of Apennine aquifers, and significant geochemical variations over long distances downstream due to mixing processes. Carbon mass-balance computations highlight the preservation of deep CO₂ signals in rivers recharged by CO₂-rich springs, making the carbon isotopic composition a reliable tracer for the groundwater-superficial water interactions. The dissolved flux of deep CO₂ was calculated using rivers data and compared with that from spring data, providing comparable estimates of deep CO₂ flux suggesting relatively low carbon loss in rivers. Rivers could provide valuable information on deep CO₂ flux and its temporal variations, even at high frequency, across large areas. Several sites, including springs and river sections, were chosen for the installation of multiparametric probes to monitor the dissolved deep CO₂ using 'easily detectable parameters' (EDP), and to correlate them with seismic activity. Ongoing studies will shed light on the variability given by the different hydrogeological periods and on the correlations between EDPs, deep CO₂ flux and seismic activity.

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Geochemical variations revealed by K-means clustering: An example from the Afar triple junction (Ethiopia)

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In the last few decades, the development of improved geochemical analytic techniques, and accessible online data repositories has led to the compilation of increasingly larger geochemical datasets. At the same time, the improvement of analytical sensitivity and precision has increased the number of variables that can be used to describe geological processes. This represents a great opportunity for detailed geochemical characterization of rocks, from the micro- (e.g., chemical zonation of minerals) to the macro-scale (e.g., discrimination of tectonic setting). On the other hand, working with large datasets and combining several variables is not always an easy task. In this regard, machine learning algorithms (MLA) represent a powerful tool to use geochemical data for e.g. the investigation of magmatic processes [Costa et al., 2023], the development of new geothermobarometers [Higgins et al., 2022], or the discrimination between tectonic settings [Petrelli and Perugini, 2016]. K-means clustering is a powerful and versatile unsupervised MLA used to create clusters (k) of multivariate data by repeatedly assigning each dataset point to the closest centroid (cluster centre). The operation is repeated, randomly relocating the centroids until the clusters minimal variance is reached. In this work, we perform K-means clustering on the entire whole rock dataset of the Afar region (Ethiopia), a rift-rift-rift triple junction where the transition from continental rifting to oceanic spreading is underway and the magmatic products are exposed subaerially. We made several selections of elements, element ratios, and/or isotope ratios and performed just as many K-means tests to investigate the principal magmatic processes (i.e., magma evolution, crustal contamination, and mantle partial melting) during rift evolution. We also performed spatial analysis of the clustered data using ArcGIS, demonstrating that K-means clustering allows discriminating spatial and temporal chemical variations within the same tectonic setting.

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Preliminary investigation of Hg in interstitial soil and free gases in a peripheral area of Mt. Etna, Sicily

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Mercury (Hg) is one of the most hazardous elements emitted into the atmosphere both from natural and anthropogenic sources. Volcanic emissions represent an important natural source of Hg in the environment known for its potential toxicity to many forms of life and for its long atmospheric residence time, which allows an efficient global distribution. My PhD project is framed within the broader context of the HERMES project (co-founded PRIN 2022) and involves the biogeochemical study of Hg on the Mt. Etna volcano. Specific aims include: determining Hg concentrations in soils and interstitial gases in soils; characterising the microbiota linked to the mercury cycle in soils; quantifying mercury emissions from the volcano's peripherals emissions; quantifying atmospheric Hg deposition fluxes. Here we present preliminary data on the outgassing of Hg from soils collected using a Lumex[®] RA-915M (Zeeman atomic adsorption spectrometer) analyser within a wide concentration range (2 to 50,000 ng m⁻³). The instrument inlet port was equipped with a three-way valve and the gas was injected into the instrument using a 100-mL syringe. The first sampling campaigns were focused on some of the degassing areas around Mt. Etna, including some of the sites of the "Etnagas" CO₂ monitoring stations network (INGV). With respect to the atmospheric background values (2-3 ng m⁻³) Hg concentration in free gases reached higher values between 264 - 9,913 ng m⁻³ in Salinelle, Aqua Grassa and Fondachello sites, highlighting an important flux of mercury to the atmosphere. Hg concentration in the interstitial gases in soils ranged from 28.7 to 57.5 ng m⁻³ in the Santa Venerina site and 52.8 to 100 ng m⁻³ in the Torre del Filosofo site. These preliminary results show that the contribution of peripheral and soil degassing with respect to the crater degassing is non-negligible and requires further investigations.

A geochemical approach to evaluate the geothermal resource in Italy: the EMOTION and IRGIE projects

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Due to its geological characteristics, Italy shows several areas with high geothermal potential, an excellent solution among renewable energy, but nowadays only the high enthalpy system of Tuscany is fully exploited. In order to provide a comprehensive information about low-to-medium geothermal resources, INGV is leading two projects funded by MUR and Regione Siciliana, respectively, i.e. EMOTION - Pianeta Dinamico (Geochemical characterization of geothermal manifestations in central-northern Italy and development of the national geothermal fluid web portal) and IRGIE (Inventario delle Risorse Geotermiche delle Isole Eolie) projects. Their aim is investigating the geochemical features of hydrothermal manifestations (thermal springs, mineral waters and gas emissions) hosted in two main areas of Italy. The EMOTION project focuses on fluids emerging in central-northern Italy, whereas the IRGIE project conducts its investigation at the Aeolian Archipelago. The methodological approach in both projects consists of a first phase of collection and review of the literature data, followed by sampling campaigns to produce new geochemical data. All data, including those chemical and isotopic parameters that are considered the most significant for geothermal prospection, entered into two similar databases. In this initial phase of the work, an analytical comparison was carried out for selected chemical species (NH_4 , SiO_2 , B, dissolved gases and $\delta^{13}\text{C}$ -TDIC) that were determined by the research groups involved in the projects by using different analytical techniques. This work shows the results of the first working phase of both projects, including the results of the analytical intercomparison.

Based on both bibliographic and original geochemical data, that will be collected during 2024, fluid circulation conceptual models will be constructed for the estimation of the theoretical geothermal potential of the selected hydrothermal systems.

Tracing a mantle component in paleofluids along the seismogenetic faults of the Irpinia region (southern Italy)

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In this study we investigate the noble gas isotopes trapped within the fluid inclusions (FIs) in calcite veins along the fault planes in the Irpinia region, which is one of the most seismogenic areas of the southern Apennines, Italy [Slejko et al., 1998]. The area is characterized by degassing of deep-sourced CO₂ [Chiodini et al., 2004], with a correlation between fluid transfer within the crust and earthquake nucleation at regional scale [e.g., D'Agostino et al., 2018; De Landro et al., 2022]. Previous geochemical investigations recognized the presence of a mantle-derived component in the degassing volatiles [Buttitta et al., 2023 and references therein].

The aim of this study is to characterize the paleo-fluids within the FIs and to compare them with fluid emitted from the current high-flux CO₂ gas emissions in the area, in order to better understand the relationship between fluids circulation and crustal deformation over time.

Results reveal that the paleo-fluids predominantly consist of a crustal component (80 to 90 %), supplemented by 10 to 20 % mantle-derived helium (indicated by a ³He/⁴He ratio of up to 1.38 Ra, Ra is the He isotopic signature in air). This He isotopes peak value is lower than typical SCLM (Sub Continental Lithospheric Mantle, 6.3 Ra) and is markedly higher than typical crustal radiogenic signature (0.01 – 0.05). These values align closely with those reported by [Buttitta et al., 2023] on free gases currently emitted in the same area (³He/⁴He from 1.27 to 1.41 Ra). The presence of mantle-derived helium in FIs, diluted by varying contributions of crust-derived ⁴He, reflects the current outgassing of deep fluids in the area that correlate with historical deformation. All this supports the hypothesis that seismic events induce rock deformation and fracturing along fault zones, there by modulating high sporadic release of He into the atmosphere. This study also provides new research points on the role of fault systems in the geochemical dynamics of the Earth's crust over time.

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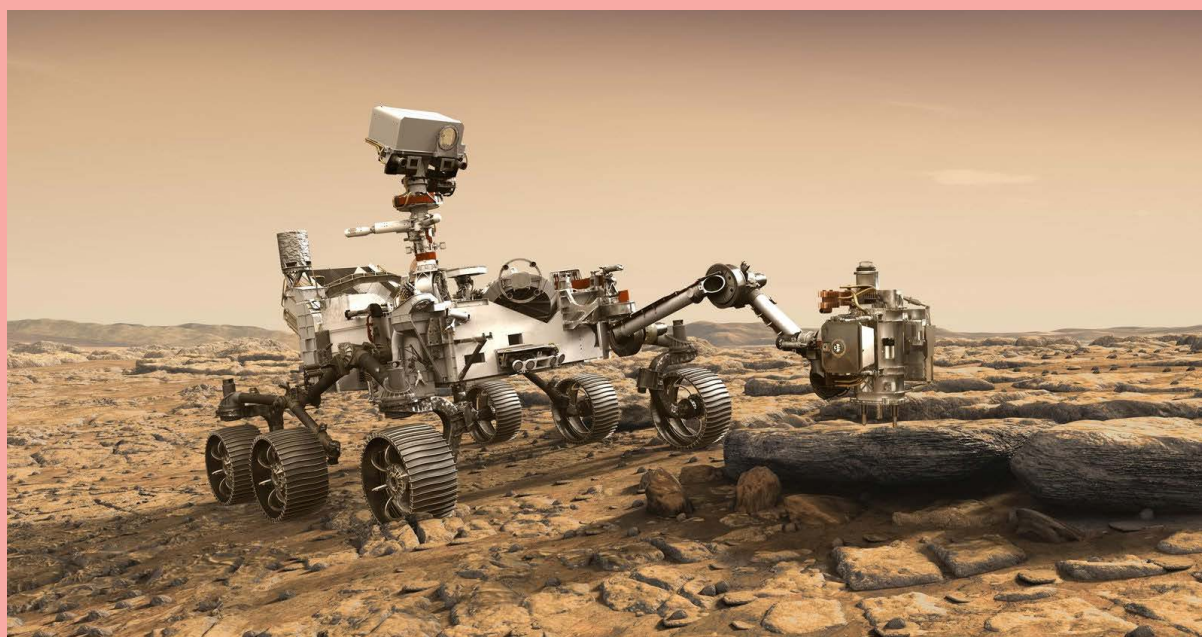
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SESSION 4 - COSMOCHEMISTRY AND PLANETARY SCIENCE

Conveners:

Nadia Balucani (DCBB, Università di Perugia), Martina Casalini (DST, Università di Firenze),
Maximiliano Fastelli (FISGEO, Università di Perugia)



Geological Map Series of Mercury: from science to science-planning of the BepiColombo mission

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A series of geological maps is being developed at a regional scale for each quadrangle of Mercury in anticipation of the ESA/JAXA BepiColombo mission [Bekhoff et al, 2020]. These maps serve to assist in identifying scientific targets and providing context for interpreting new data by addressing outstanding questions about the surface evolution of the planet [Rothery et al., 2020]. They are created at an average mapping scale of 1:600,000 through photogeologic interpretation of NASA MESSENGER/MDIS end-of-mission basemap mosaics [Denevi et al., 2018]. Following USGS planetary mapping guidelines and the Horizon 2020 Planmap project standards, the maps are then published at an output scale of 1:3,000,000. By 2022, eight out of fifteen quadrangles (H-02, H-03, H-04, H-05, H-06, H-10, H-13, H-14) had been completed and published. To ensure consistency, boundaries of published maps are being reviewed and updated to create a continuous digital geological map now accessible on the Mercury Quickmap website. The current merged quadrangle maps provide a coherent and uninterrupted view of Mercury's geological framework, covering over 50% of the planet. The remaining seven quadrangle maps are scheduled for completion by the end of 2024 (H-07, H-08, H-09, H-11, H-12, H-15), with only H-01 expected to be finalized in 2025, just before BepiColombo's Mercury orbit insertion.

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FRESCO, a Python open-source tool to map, select, extract and analyze CRISM spectral data

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Hyperspectral data provide essential information on the surface composition of terrestrial planets. On Mars, these data are provided by CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) [Murchie et al., 2007], a hyperspectral camera onboard MRO (Mars Reconnaissance Orbiter). CRISM covers a spectral range going from 400 to 4000 nm, with a spectral resolution of 6.55 nm/channel and a spatial resolution up to 18.4 m/px. CRISM data products include MTRDRs (Map-Projected Target Reduced Data Records) [Seelos et al., 2016], that are projected onto the surface and are cleaned from noisy stripes. The two main CRISM MTRDR subproducts are the hyperspectral datacube and the spectral parameter datacube, composed of 60 spectral parameters [Beck et al., 2014].

While the commercial software ENVI© is often used to perform the spectral analyses, it is not tailored on these dataset [Baschetti et al., 2024] and have some user costs. We present here a free open-source tool written in Python called FRESCO (Flexible RGB Extraction and Spectra Comparison for Observations), which allows the use of CRISM MTRDR data.

The software can create RGB maps and select Regions Of Interest (ROI) from which extract and analyze the spectral data. The supported analyses range from descriptive statistics and pre-processing methods to more complex analyses, like Machine Learning (ML) for automatic detection of absorption lines or ML-driven Multi Gaussian Models (MGM) [Sunshine et al., 1990] for spectral unmixing. The ML models are as transparent as possible to ensure reproducibility and interpretability. FRESCO also support georeferenced RGB maps and spectra to be exported to ArcGIS©/QGIS for comparison with other CRISM reference or laboratory spectra [MICA, 2019]. In support of FRESCO, a case study about the CRISM target FRT00009B5A at Kai crater in Meridiani Planum is presented. The target choice is motivated by the morphological and compositional complexity [Baschetti et al., 2023], showcasing FRESCO utility in a complex scenario requiring detailed analyses of the geological context, evolution, and processes.

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A journey from the Moon and back through petro-mineralogical and geochemical investigation of lunar meteorites

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The composition of the lunar crust provides key information on the petrological evolution of the Moon. Compared to the analyses of Apollo samples, which restricted the typologies of lunar rocks to Ferroan Anorthosites (FAN) and Mg-suite, data from lunar meteorites have shown the presence of a more widespread compositional range. To need of explaining this compositional variability led to a re-evaluation of the Lunar Magma Ocean model, although the “pristine” character of lunar meteorites remains a topic of debate. In the framework of the MELODY project, we investigated three lunar meteorites: i) NWA 13859 a polymictic feldspathic breccia (made up by clasts of anorthosite, gabbroic anorthosite, troctolite, anorthositic norite, gabbroic norite); ii) NWA 8687 a monomictic breccia classified as troctolite and iii) NWA 14188, a basaltic breccia. Major and trace elements of the mineral phases and the matrix glass were analysed by Electron Microprobe (EMPA) and Laser-Ablation ICP-MS (LA-ICP-MS). The mineral composition of the three lunar breccias agrees with the lunar meteorite fields with only few clasts of the polymictic breccia (gabbroic anorthosites and anorthositic norites) falling in the field of FAN, whilst gabbroic norites reach compositions typical of Mg-rich suite. Even more mafic is the composition of the monomictic breccia, straddling the boundary between MAN and Mg-suite, while the basalt breccia has a mineralogical composition similar to that of FAN. Major and trace elements compositions of plagioclase and pyroxene vary in the range of previous data on feldspathic meteorites, arguing against simple fractional crystallization from a single Lunar magma Ocean. Worth of note is the glassy matrix that although resembling an average of the mineral composition, sometime preserve the exogenous fingerprint related to the impactor that blasted the meteorite off the Moon, or to micrometeorites associated with regolith gardening and maturation.

Reflectance spectra of mascagnite and salammoniac minerals with varying viewing geometry

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Ammonium-bearing minerals have been hypothesized on icy planetary bodies like Pluto and Ceres [De Sanctis et al., 2016; Cruikshank et al., 2019]. NH_4^+ -minerals may be linked to upwelling of ice from subsurface oceans [Cruikshank et al., 2019]. Surface roughness, topography, and morphology affect the reflectance spectra of Solar System bodies due to observation geometries [Cruikshank et al., 2015]. This study analyzes the effects of viewing geometry variations on near-infrared reflectance spectra of mascagnite- $(\text{NH}_4)_2\text{SO}_4$ and salammoniac- NH_4Cl powder samples [Fastelli et al., 2023]. Bi-directional reflectance spectra were collected in the 1 - 4.2 μm range at 3 incidence (i) angles ($i = 0^\circ, 30^\circ, 60^\circ$) and 9 emergence (e) angles between -70° and 70° . The spectra were collected using SHINE bidirectional reflectance spectro-goniometers at the CSS facility of the IPAG laboratory as part of the Europlanry project. Experimental investigation focused on NH_4^+ absorption bands at $\sim 1.09, 1.32, 1.62, 2.04, 2.2,$ and $3.05 \mu\text{m}$. Changes in observation geometry affected absorption band parameters, reflectance values, and spectral slope but not band positions. Band area and depth showed high variability for $i \geq 30^\circ$ and $e > \pm 40^\circ$. Band depth and area depended strongly on incidence angle, up to 60° , with moderate variation with emergence angles. The $\sim 3 \mu\text{m}$ absorption band became less saturated at $\pm 70^\circ$ emergence angles, showing a general trend of spectral bluing with changing observation geometry. This dataset contributes to understanding NH_4^+ -bearing minerals on icy bodies for present and future space missions. Identification of NH_4^+ -minerals impacts understanding of their thermal evolution, geophysical internal models, geological phenomena like cryovolcanism, and implications for biological activity.

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Theoretical insights on the S(1D) + H₂O reaction and implications on the chemistry at the surface of ice in extraterrestrial environments

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Over the last decade, there was an important advance in the comprehension of formation and destruction routes of the most common interstellar chemical species. However, a significant lack of knowledge concerning the chemistry of other minor species is still present, often due to the limited amount of both computational and experimental data. [Ceccarelli et al., 2023] In this contribution, the possible role of the electronically-excited sulphur S(1D) in the chemistry of interstellar or cometary ice has been explored through a theoretical characterization of the S(1D) + H₂O reaction in the gas-phase and in the presence of a cluster of four and eighteen water molecules. All the stationary points of the investigated potential energy surface (PES) were optimized at the density functional (DFT) level of theory, using the B3LYP functional [Becke, 1992] and the correlation-consistent valence-polarized basis set aug-cc-pVTZ [Dunning, 1989] basis set, augmented with a tight d function on sulphur atoms [Dunning et al., 2001]. The presence of the 4- and 18-water-molecules cluster drastically changes the reaction mechanism since the SO + H₂ channel, which is the only open channel in the gas-phase reaction, cannot occur due to the hindrance caused by the H-bonds between the involved reaction intermediates and the water molecules of the cluster. At the same time, a global reduction of the energy content with respect to the reactants makes the H-displacement channels leading to HSO and HOS allowed from a thermodynamic standpoint, whereas they are endothermic, thus unfavored, for the isolated system. Notably, in the case of 18-water-molecules cluster, an enzyme-like effect of the cluster shows that the reaction pathways are consistently favored because of the substantial reduction of the energy barriers connecting the minima of the potential energy surface (PES). Overall, the ice matrix has been predicted to stabilize the reactive intermediates HSOH and H₂SO. Further work is necessary to simulate the ice environment better and confirm these preliminary results.

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A combined investigation of the reactions of N(²D) with small aromatic compounds and implications for the chemistry of Titan's atmosphere

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The reactions of atomic nitrogen in its first electronically excited state, ²D, with different organic molecules are considered pivotal processes for the formation of new species holding a novel C-N bond in the atmosphere of Titan [Balucani et al. 2023, Mancini et al. 2023]. Titan, the largest moon of Saturn, is indeed characterized by a nitrogen-rich atmosphere, with molecular nitrogen accounting for more than 94% of the total composition, followed by methane and many other saturated and unsaturated hydrocarbons. The observation of nitriles and N-rich organic macromolecules clearly indicates the involvement of nitrogen chemistry, promoted mainly by dissociative photoionization and/or photodissociation of N₂ [Loison et al. 2015, Vuitton et al. 2019]. Those processes form nitrogen atoms both in the ground ⁴S and in the ²D, which is a metastable state with a long radiative lifetime. In the present contribution, a combined theoretical and experimental investigation of the reactions of N(²D) with aromatic compounds, namely benzene (C₆H₆), pyridine (C₅H₅N) and toluene (C₆H₅CH₃) is presented. Theoretical predictions, obtained through electronic structure calculations of the potential energy surfaces and statistical estimates of product branching fractions, supported by experimental results (obtained using the crossed molecular beam technique) allowed to elucidate the reaction micro-mechanism and unveil the main products. Our results are expected to have a significant impact on the gas-phase chemistry of Titan's atmosphere and will be included in the photochemical models.

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The role of oxygen atoms in space organic chemistry: the case of $O(^3P, ^1D) +$ small aromatics reactions

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Polymeric materials have emerged as crucial components in the aerospace industry, but their use is challenged by the exposure to atomic oxygen (AO). AO erosion has been recognized to be a critical hazard for polymers exposed to the conditions of the Low Earth Orbit, where most satellites orbit. Similar processes can involve refractory forms of carbon (amorphous graphite or large polycyclic aromatic hydrocarbons) that are abundant in our galaxy. The mechanism is still in need to be characterized at the atomistic level. For this reason, we have started a systematic investigation of the reactions of AO with prototypical aromatics, namely, benzene (C_6H_6) [Vanuzzo et al., 2021], pyridine (C_5H_5N) [Recio et al., 2022], and toluene (C_7H_8) [Balucani et al., 2024]. We have exploited the crossed molecular beam technique to unveil the primary products, their branching fractions (BFs), and the reaction micro-mechanism. The interpretation of the experimental results has been supported by theoretical computations of potential energy surfaces and product BFs. For the reactions between $O(^3P, ^1D)$ and C_6H_6/C_5H_5N , two main groups of mechanisms were observed: (i) the H-displacement channels and (ii) the ring-contraction channels, leading to CO. The presence of the N atom in the aromatic ring of C_5H_5N increases the probability of the ring-contraction mechanism. The presence of a CH_3 group in the C_7H_8 molecule allows preserving the six-member aromatic ring.

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Platinum-Group Elements (PGEs) determination in Canyon Diablo meteorite

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Canyon Diablo (CD) meteorite, named after the impact crater in Arizona, was classified as an iron meteorite belonging to the IA group, Main Group (MG), as formed by a large contribution of chondritic processes [Walker, 2016, Worsham et al., 2016]. Although the Meteor Crater is widely studied [e.g., Kring, 2017], the literature dealing with the meteorite is sporadic and mainly focused on the silicate content and calcite veins [e.g., Hilton et al., 2020], indeed, the main body was almost completely vaporized in the impact and most of the few ejecta left melted within the surrounding lithologies. This contribution aimed to chemically characterize two Meteor Crater fragments, one (CdD₁) already certified as a CD piece and one (CdD₂) bought from an e-commerce network without any guarantees about the declared origin. The study focused on bulk and *in-situ* analyses of minor and trace highly siderophile elements (HSEs) and platinum-group elements (PGEs), combined with bulk C isotopic ratios measured *in-situ* on the individual block, not on powder, such analytical procedure found no records of analogues in the literature. For both samples, the main mineralogical constituents were taenite-kamacite and rare sulfides. In addition, the two fragments showed the same major and trace element chemical composition, with Fe 91.3-91.6 wt.%, Ni 7.60-7.87 wt.%, and Pt 1.13-1.40 ppm, Au 2.58-6.74 ppm, in agreement with literature values for group IA iron meteorites [Hirata & Nesbitt, 1997], and for CD [Wasson & Ouyang, 1990, Hilton et al., 2020]. Therefore, both CdD₁ and CdD₂ are fragments derived from the same meteoritic body. Finally, it is important to note that, compared with the IA-MG group, CD fragments have lower Ni and Au contents, thus they could be classified as belonging to the subgroup IAB sLL.

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