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MISCELLANEA INGV

Abstract Volume

1st Congress of Società Geochimica Italiana “From theoretical to applied geochemistry”

July 5-8, 2022 | Genova, Italy

ISTITUTO NAZIONALE
DI GEOFISICA E VULCANOLOGIA

69

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Editors: Sergio Calabrese[1,2], Giovannella Pecoraino[2], Monia Procesi[3] and Orlando Vaselli[4,5]

[1]Università degli Studi di Palermo, Dipartimento di Scienze della Terra e del Mare (DiSTeM), Italy
[2]INGV | Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italy
[3]INGV | Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Roma 1, Italy
[4]Università di Firenze, Dipartimento di Scienze della Terra, Firenze, Italy
[5]CNR | Istituto delle Geoscienze e delle Georisorse (IGG), Firenze, Italy

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Mauro Masiol	(Università Ca'Foscari Venezia)
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Orlando Vaselli	(Università degli Studi di Firenze)
Stefania Venturi	(Università degli Studi di Firenze)
Marino Vetuschi Zuccolini	(Università di Genova)

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Foreword

Dear Participants,

It is a pleasure and an honor to have you here attending the very first Congress of the Italian Society of Geochemistry: *From theoretical to applied geochemistry*. This meeting also has another important meaning. All of us are here in the Palazzo Rosso of the Municipality of Genoa to celebrate the outstanding scientific and didactic activity of Prof. Giulio Ottonello who has dedicated his life to geochemistry producing milestone papers and a book (“*Principles of Geochemistry*”) that is also used in the U.S.A. universities. It is our hope that our young scientists (Ilaria Fuoco, Caterina Gozzi and Francesco Magi), who are awarded by our Society for their PhD work, will follow the path signed by Prof. Ottonello in their respective fields.

The congress has had an unexpected positive result since we thought that the 2-years long (so far) pandemic, during which we were forced to postpone this event, would negatively have affected the participation. Instead, more than 80 abstracts were submitted and various key-note and invited speakers accepted to be present for giving talks on their most recent discoveries in different disciplines of Geochemistry. This congress has indeed been divided into four distinct, though intimately linked, sessions, the first of which, named Thermodynamics in Geochemistry, hosts several prominent international and national scientists (Enrico Bonatti, Bartolomeo Civalleri, James Connolly, Jibamitra Ganguly, Carlo Gatti, Pascal Richet and Surendra Saxena) who are intervening with specific talks to celebrate the career and their friendship with Prof. Ottonello who is going to give a *lectio magistralis*. Environmental Geochemistry, Isotope Geochemistry and Fluid Geochemistry are the other three sessions into which the congress is articulated. The key-note lectures will be given by Alessandro Aiuppa, Giovanni Chiodini and Riccardo Petrini while the invited speakers are Gianluigi Ortensi, Eleonora Regattieri and Roberta Parigi, respectively.

This event has a relatively long story, and several colleagues and friends were involved. First of all, Donato Belmonte and Marino Vetuschi Zuccolini (who also acted as conveners of the Thermodynamics in Geochemistry session) are warmly thanked for the organization and logistic of the congress. They were helped by the other members of the Organizing (Stefano Caliro, Francesco Capecchiacci, Enrico Dinelli, Barbara Nisi, Stefania Venturi) and Scientific (Sergio Calabrese, Paola Iacumin, Mauro Masiol, Michele Paternoster, Giovannella Pecoraino, Monia Procesi, Barbara Stenni, Daniela Varrica) Committees. The abstracts reading and the program of the event were drawn up by the convenors of the other three sessions: Carmine Apollaro, Enrico Cannaò, Rosa Cidu, Luigi Dallai, Kyriaki Daskalopoulou, Francesco Frondini, Barbara Nisi, Elisa Sacchi and Giancarlo Tamburello. The Municipality of Genoa is thanked for giving us the opportunity to host the event in the main hall of Palazzo Rosso.

A special thanks is to the President of INGV (Carlo Doglioni) who strongly supported and sponsored the event. Sergio Calabrese, Giovannella Pecoraino and Monia Procesi edited this INGV Miscellanea, Francesca Di Laura was the incredible designer of the graphics used in this congress and Giovannella Pecoraino realized the T-shirts, the bags and all the other “INGV-branded” gadgets. Our community thanks their help and dedication. Private companies (ThermoFischer, Metrohm, Pollution Analytical Equipment, Thaeren, and Encotech) are kindly acknowledged for sponsoring the congress.

Now, it is time to enjoy the congress with the hope to organize this event every two years.

Orlando Vaselli

Awards

PREMIO TONANI

***

Geochemical modelling of natural contaminants in groundwaters and their removal by membrane processes

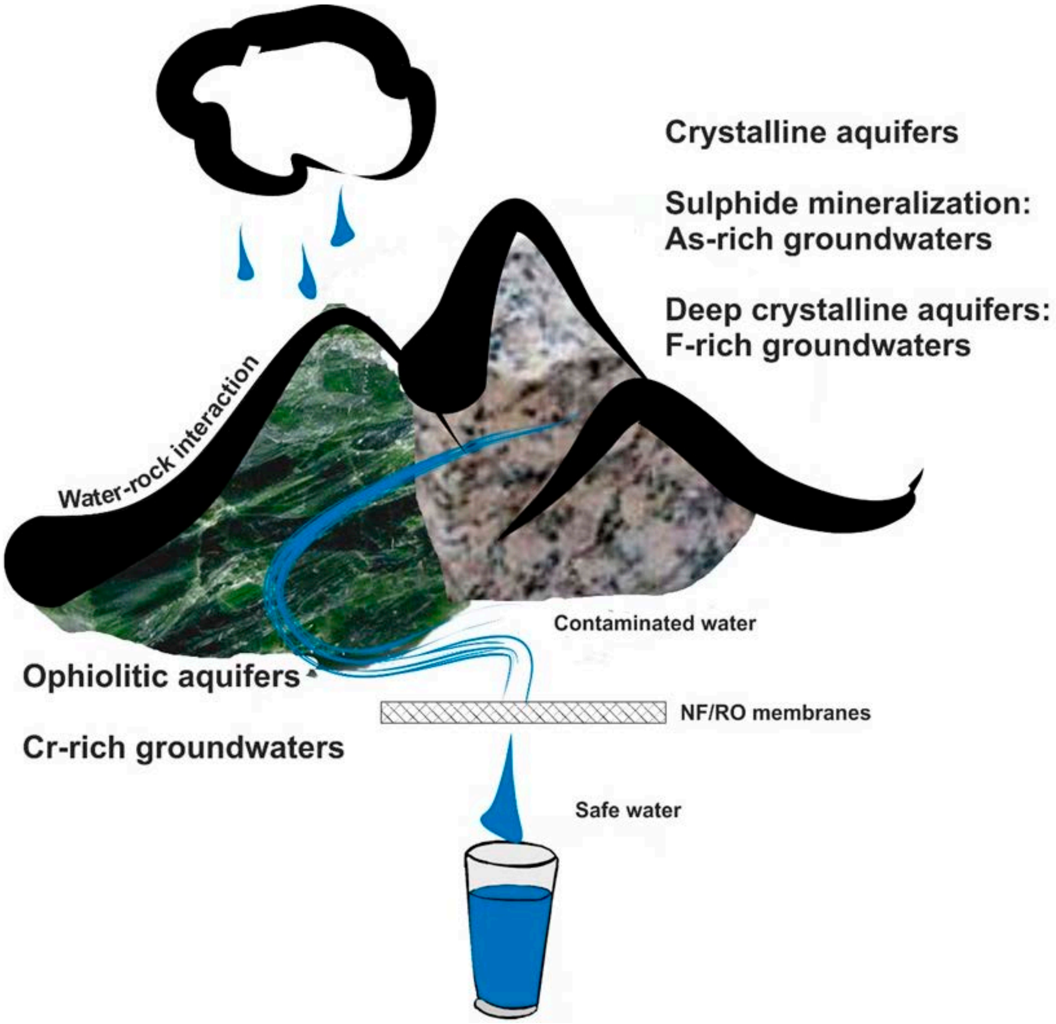
Ilaria Fuoco

Università della Calabria, Dipartimento di Biologia, Ecologia e Scienze della Terra, Cosenza, Italia

Keywords: Reaction path modelling; Inorganic pollutants; Calabria (southern Italy)

The aim of present study was to study the rock-to-water release of some inorganic pollutants (As, F and Cr) in groundwaters of different Italian areas, and select suitable membrane technologies for their removal based on the acquired geochemical knowledge. To understand the high As and F concentrations detected in some areas of Calabria Region, three different reaction path modeling exercises of granite dissolution were performed, reconstructing the processes which occur: (i) in shallow and relatively shallow crystalline aquifers in which no As and F anomalies were observed; (ii) in As-rich areas, coupling the reaction path modeling of granite dissolution with the simulation of the adsorption of dissolved As onto precipitating crystalline and amorphous hydrous ferric oxide (HFO); (iii) in deep crystalline aquifers where high F concentrations were detected. Several water samples discharging from the crystalline aquifers of the Calabria region were used to fix the boundary conditions as well as to validate the outcomes of geochemical modeling. The results are in agreement with the analytical data, reproducing satisfactorily the water-rock interaction processes occurring during the travel of meteoric waters from shallow to deep crystalline aquifers, hosted both in granite rocks without mineralizations and in mineralized granites. To understand the mineralization process of Cr(VI)-rich groundwaters, the attention was focused on the water-rock interaction processes occurring in the main ophiolite aquifers of Italy. Reaction path modelling of serpentinite dissolution was performed varying the $Fe_2O_3/(FeO + Fe_2O_3)$ weight ratio of serpentine and reproducing the analytical concentrations of relevant solutes, including Cr(VI), in the Mg-HCO_3 groundwaters hosted in the ophiolite aquifers of Italy. The occurrence of geogenic Cr(VI) in these groundwaters appears to be potentially controlled by the oxidation of trivalent Cr to the hexavalent redox state, driven by the reduction of trivalent Fe to the divalent redox state. In fact, trivalent Fe is the only oxidant present in suitable amounts in serpentinite rocks. However, to validate these outcomes, the redox state of Fe in serpentine minerals was measured in five serpentinite samples coming from the main ophiolite areas of Italy. The electron energy-loss spectroscopy (EELS) combined with transmission electron microscopy (TEM) was selected as most suitable analytical technique allowing to obtain a good qualitative and quantitative information on iron redox speciation. The performed analyses provided in-depth knowledge on nanoscale structures of the studied samples and showed that Fe(III) represents from 75 to 85 % (median values) of total iron, further supporting the findings of geochemical modeling. Finally, some As-, F- and Cr-rich groundwaters were selected from the previous data collections. Based on the acquired geochemical knowledge several type of commercial nanofiltration/reverse osmosis membranes, not already tested in the pertinent literature, were selected depending on the type of application. Their efficiency was evaluated in terms of As, F and Cr rejection, water production and feed composition. The other main ions that contribute to water chemistry were also taken into account to evaluate the possible intended use of the considered waters after the treatments. Satisfactory results were obtained for each specific case of contamination. Moreover, an innovative membrane with absorbent capacities against As(III) and As(V) species was developed and the preliminary results are quite promising. Summing up, the findings obtained in this work are useful for the understanding of the rock-to-water release of the chemical elements of interest and their fate in natural waters. Moreover, the treatment of natural As, F, and Cr-contaminated groundwaters improved the knowledge and the data availability for future scientific and application developments in similar geological settings worldwide.

Graphical Abstract



PREMIO PANICHI

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Isotope Geochemistry of rainfall, thermal and non-thermal waters from the Mt. Amiata area (northern-Central Italy)

Francesco Magi

Università di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia

Keywords: Stable isotopes; Water geochemistry; Mt. Amiata (central Italy)

The purposes of this research, were to: i) build up the first Local Meteoric Water Line (LMWL); ii) better characterize and compute the average recharge areas of the shallower hydrogeological environments related to either the homonymous Mt. Amiata volcanic or the carbonate aquifers; iii) determine radiometric age of the waters; iv) investigate the influence of the climate change on the shallow groundwater bodies; v) understand the chemical isotopic relationships between different shallow or deep fluid end-members to explore their hydrogeological pathways within the geological structures as well as the related water quality of the spring waters.

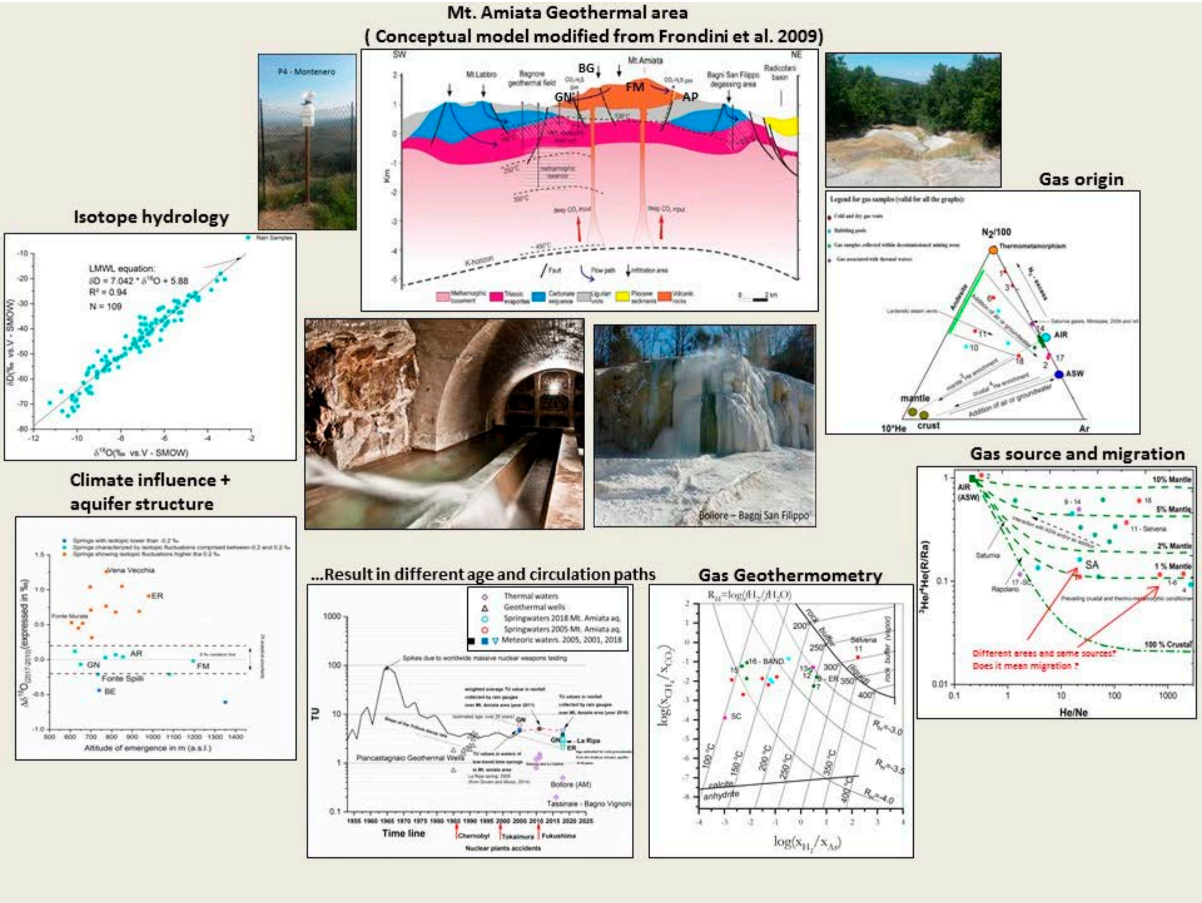
A network of passive rain gauges was installed to collect rain water samples and measure rainfall levels. More than 128 rain water samples were retrieved and analyzed for the stable isotopic composition as well as for tritium activity. Spring water samples (126) with different chemical composition were analyzed for main, minor, trace and isotope chemistry. A sampling campaign was also conducted to collect gas samples (18) from the main gas emissions in the surroundings of the Mt. Amiata volcano (here included some dismissed mining areas). Particularly, due to their highly impacting potential on both the air quality and human health, it was paid great attention in providing an updated census of these natural punctual and/or diffuse emissions in the area. A detailed study was thus carried out by noble gas isotopic tracers to understand whether the geological structures were affecting and/or favoring the gas release mechanisms to the surface. This constitutes the very first work performed in the area and involving a full scan of NG nuclides, ranging from He (helium) to Xe (xenon).

The main results can be summarized, as follows: i) the preliminarily computed LMWL resulted to be in accordance with precipitation in Central Italy; ii) being the vertical isotopic gradient for oxygen set around -0.19‰/100 m, the average recharge altitudes were computed in about 1200 m a.s.l. and around 1000 m a.s.l. for waters from Mt. Amiata and the regional aquifers, respectively; iii) the Mt. Amiata aquifer responds with a lag-time of a few months to relevant inputs of meteoric recharge and shows likely different patterns of circulation; iv) Mt. Amiata *significant groundwater body* appeared to reflect variations likely due to climate-change as "isotopic-enrichment" was observed especially for $\delta^{18}O$ over the last decade.

From a compositional perspective the following hydro-geochemical facies were recognized for the analyzed waters: **Group A**: Ca(Na)-HCO_3 and Na(Ca)-HCO_3 cold waters from the Mt. Amiata volcanic aquifer; **Group B**: cold Ca(Mg)-HCO_3 emerging from the regional carbonate aquifer; **Groups C/D**: Ca-SO_4 from thermal or bubbling waters.

The gas samples showed a CO_2-dominant composition, followed by N_2 and CH_4. The study of the stable isotopic gas signatures based on the coupled usage of mainly $\delta^{13}C$-CO_2 $\delta^{13}C$-CH_4 along with specific NG ratios pointed out a likely primary crustal-thermo-metamorphic origin of these fluids to which small variable contributions of metasomatically enriched-mantle CO_2 seem to be added. This is well consistent with the thermo-metamorphic conditions that should likely be encountered even today, affecting the Palaeozoic host-rocks, at the outer interface of the buried Mt. Amiata pluton and at the shallower levels where the geothermal reservoir is hosted. The log (XH_2/XAr) vs. log (CH_4/CO_2) geo-thermometers evidenced deep fluid equilibration at around 300°C. This PhD work has dealt with shallow and deep-seated fluid geochemistry. Hydraulic relationships between the shallow and deep aquifers should further be deepened by both isotopic and chemical means. Particularly, the calibration of an accurate and tritium-based circulation model suitable to be applied to the Mt. Amiata system is therefore highly recommended.

Graphical Abstract



PREMIO TONGIORGI

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Weathering and transport processes investigated through the statistical properties of the *geochemical landscapes*: the case study of the Tiber River basin (Central Italy)

Caterina Gozzi

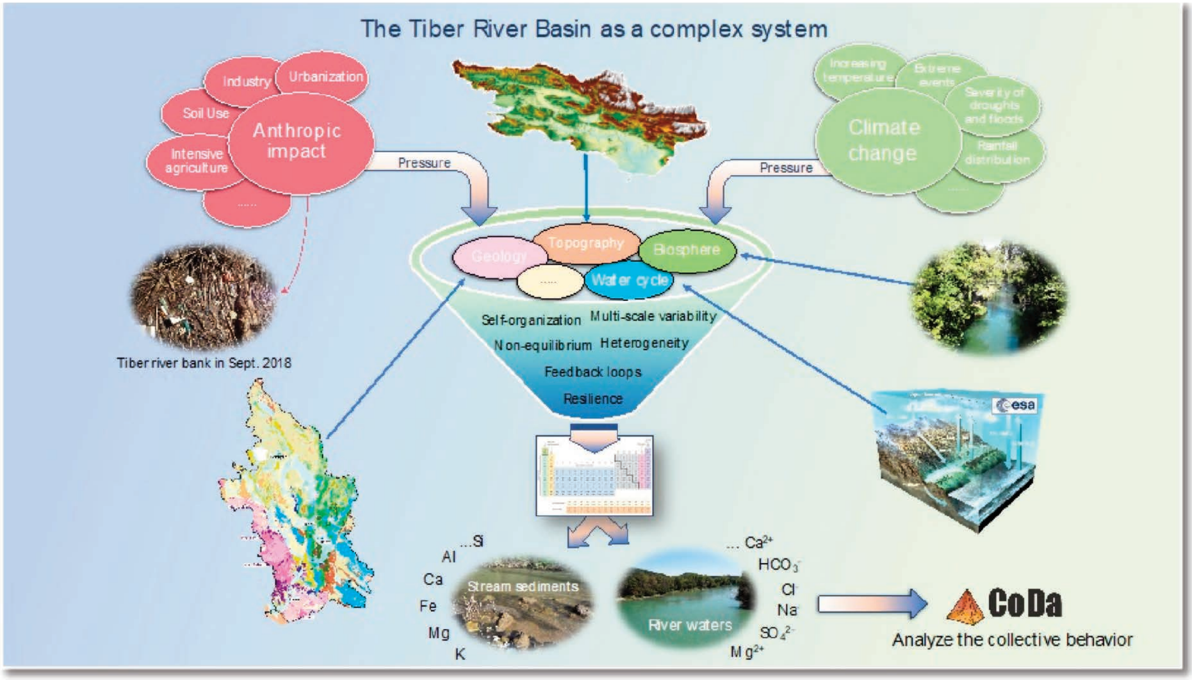
Università di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia

Keywords: River geochemistry; Geochemical landscapes; Tiber River basin (central Italy)

Water and sediment transported and distributed within a river catchment represent sentinel variables able to monitor the interactions between litho-hydro-eco-atmospheric processes at different scales. This research illustrates the results of a three-year Ph.D. project concerning the study of the geochemical landscapes of the Tiber River basin (TRB), the largest catchment in central Italy (17,156 km^2). The basin is mostly characterized by terrigenous deposits in its upper part, the carbonatic Apennine ridge towards south-east and potassic and ultra-potassic volcanic complexes in the south-western area. This heterogeneous geological environment coupled with a significant presence of anthropic activities has made the TRB, a catchment that has received very little attention so far, the ideal case of study to evaluate the nature of the geochemical variability. A total of 222 water samples from the Tiber River and its tributaries were analyzed under different flow conditions. Additionally, the chemical composition and magnetic susceptibility of 57 stream sediments were examined to assess chemical-physical weathering processes and monitor possible pollution sources. Data were analyzed using a combination of multidisciplinary approaches and statistical methods developed within the Compositional Data Analysis Theory: *i)* cascade approach of robust compositional biplots to reveal different scales in the variability structure of the data; *ii)* applications of the robust Mahalanobis distance between pairs of multivariate observations to detect compositional changes in the water chemistry through the TRB and along the main course (iterative method); *iii)* creation of a sequence of isometric log-ratio coordinates, called Principal Balances (PBs), which successively maximizes the explained variance in the dataset and its application to evaluate the effects of flood and drought conditions; v) analysis of PBs density distributions to identify the presence of basins of attraction and assess system resilience to change in the light of recent methods used for the detection of early warning signals in ecology and climate science and, vi) robust factor analysis to examine water-sediment interaction processes. Furthermore, mutual relationships between the morphological attributes of the contributing areas, delineated using a GIS-based elaboration, and the Total Dissolved Solids (TDS) of river waters at the outlets were examined. As a result, the geochemical landscapes of the TRB were determined, revealing a high level of structural complexity characterized by a multi-scale variability related to water-rock interaction and denudation processes and to the influence of human activities (e.g., agricultural practices). The Tiber River exhibits a high resilience to changes in its early to medium course, by contrast, a low resilience characterizes its low course which displays, after the Nera confluence, a critical shift towards an alternative state (composition). The new proposed methods and graphical numerical elaborations provided an enhanced comprehension of the adaptive capacity of the TRB to changing conditions (e.g., seasonal effects, compositional shifts), improving system predictability in the face of potential pollution events or climatic variations. In addition, the analysis of relationships between the TDS

and the landscape properties of the watersheds revealed, for the TRB, a pivotal role of elevation and slope patterns. This research opens new perspectives for studying complex river systems from a holistic point of view, contributing to a deeper understanding of the universal behavior and natural laws that control the resilience of water systems.

Graphical Abstract



SESSION 1 - GEOCHEMICAL THERMODYNAMICS

Conveners:
Donato Belmonte (Università di Genova), Marino Vetuschi Zuccolini (Università di Genova)

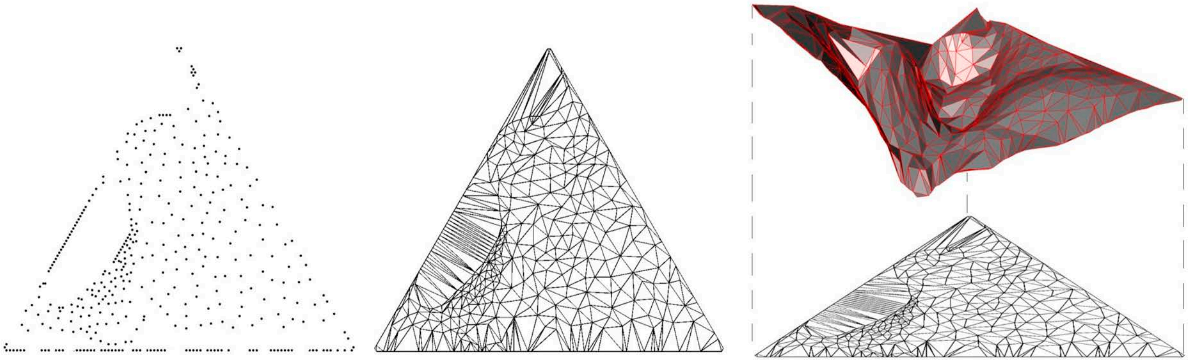


Figure caption: Multi-component phase diagrams simulated by ab initio computational thermodynamics.

Graphics design by Donato Belmonte

Ab initio phase diagrams

Giulio Ottonello

Università di Genova, Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Laboratorio di Geochimica, Italia

Keywords: *Ab initio* phase diagrams – Silicate melts – *IEFPCM*

From the first observations that the polymerization extent of a silicate melt is directly related to the electron density of the inner orbitals of the acceptor, affected by the donor's pressure (i.e. *Nephelauxetic effect*; Duffy and Ingram, 1970,1971] to the appraisal of the effect of ad-atoms on polymeric structures [Gatti et al., 2012] and the consciousness that these substances may be treated as simple ionic solvents in the framework of *IEFPCM* (Integral *Equation Formalism of the Polarized Continuum Model*) [Tomasi et al., 1999; Ottonello and Richet, 2014], it appears finally at hand the possibility of determining quantitatively *ab-initio* the energy of this class of substances. The build-up of phase diagrams (i.e. the Schreinemakers T-X projections of the phase stability limits at liquidus, solidus and subsolidus conditions) requires however a stringent *first-principles* analysis of all the crystalline polymorphs virtually nucleating in the system [Belmonte et al., 2017].

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A “Maverick” Geochemist: Giulio Ottonello

Enrico Bonatti[1,2]

[1]Columbia University, Lamont Doherty Earth Observatory, New York, NY, USA
[2]Istituto di Scienze Marine (ISMAR) Consiglio Nazionale delle Ricerche (CNR), Bologna, Italia

Keywords: Principles of Geochemistry; Giulio Ottonello; Maverick scientists

The majority of scientists are generally viewed as following in their work an “orthodox” Cartesian mode of logical deductive reasoning. However, a small minority also exists of “maverick” scientists, who work mostly by non-systematic intuition. Both approaches are important; however, they are rarely found in the same person. Giulio Ottonello is one of them: he has been able to advance greatly the field of Geochemistry by combining the systematic “orthodox” approach with that of an imaginative “maverick”. His “Principles of Geochemistry”, published already 20 years ago, is still very valid as a major “orthodox” synthesis. But then many of his papers are based on creative original “maverick” intuitions. I have known Giulio for many years, and we shared a few adventures. Here I will mention only our field work together on the beautiful desert island of Zabargad, that exposes uplifted upper mantle and lower crust of the Northern Red Sea, where a new ocean is being created by the separation of Arabia from Africa.

Ca, Al-rich hydrogarnet thermodynamics and phase stability relations: preliminary results

Nicola Campomenosi[1,2], Donato Belmonte[2,3]

[1]*University of Hamburg, Department of Earth Sciences, Hamburg, Deutschland*
[2]*Università di Genova, Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Italia*
[3]*Museo Nazionale dell'Antartide (MNA), Sezione di Genova, Italia*

Keywords: Ca, Al-rich hydrogarnet; *Ab initio* phase diagrams; Natural and CASH model systems

The incorporation of H and/or water in nominally anhydrous minerals has a notable effect on their physical properties with important implications in geophysics and geochemistry [Smyth et al., 2006]. Ca,Al-rich hydrogarnet [$Ca_3Al_2(SiO_4)_{3-x}(H_4O_4)_x$, with x = 0-3] is a common mineral phase in natural samples and it is one of the main rock-forming minerals in rodingite and metamorphic equivalent [Bach and Klein, 2009; Haws et al., 2021]. Nevertheless, reliable thermodynamic data that allow us to take the hydrogarnet into account when performing phase equilibria modelling are still incomplete. In this contribution we present, for the first time, a complete set of ab initio simulations determining the heat capacity, Grüneisen parameters, thermal expansion and isothermal bulk modulus of the Si-free end-member katoite [$Ca_3Al_2(H_4O_4)_3$] in a broad range of P-T conditions. Our calculations are in excellent agreement with the few experimental data available so far [Olijnick et al., 1991; Geiger et al., 2012] and can be used to fill the gap in the thermodynamic database. Then, by exploiting ab initio data, we tentatively consider the thermodynamic stability of this phase with respect to the solid mixture between the katoite and grossular end-members in both natural and CASH model systems. Our aim is putting this mineral phase into a new level of consideration about the possible implication that it may have on the storage and re-cycling of water during metamorphic processes in the Earth interiors.

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Computational discovery of novel inorganic materials under pressure via genetic evolutionary algorithms

Davide Ceresoli[1], Francesca Menescardi[2] and Donato Belmonte[2]

[1]*Istituto di Scienze e Tecnologie Chimiche (SCITEC), Consiglio Nazionale delle Ricerche (CNR), Milano, Italia*
[2]*Università di Genova, Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Italia*

Keywords: Crystal Structure Prediction (CSP); USPEX algoritm; Trivalent dinitrides; CaO-SiO_2 polymorphism

Computational materials discovery can be called one of the main goals of theoretical/computational materials science. Since the crystal structure determines the physical and thermodynamical properties of a material, one must first be able to predict crystal structures. Crystal Structure Prediction (CSP) consists in finding the most stable and probable crystal structures of a compound given only the elemental composition. For many years CSP has remained a formidable challenge [Gavezzotti, 1994]. The situation changed in 2002-2006 when meta-dynamics [Laio and Parrinello, 2002] and evolutionary algorithms where were developed [Oganov and Glass, 2006]. These methods, when coupled to first principles DFT calculations, proved successful in predicting novel materials with uncommon structure and stoichiometry under pressure. Nowadays CSP is widely accepted as an essential instrument of modern research. In this work we will discuss the evolutionary algorithm USPEX [Glass et al., 2006] (which is one of the most widely used CSP method) and show two applications: the first is the prediction of trivalent dinitrides [Menescardi et al., 2021] than can be synthesized under pressure. The second is the exploration of the polymorphism of the CaO-SiO_2 binary at ambient and at high pressure.

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Quasi-harmonic *ab initio* calculations of periodic systems: the case of molecular crystals and porous materials

Bartolomeo Civalleri

Università di Torino, Dipartimento di Chimica, Italia

Keywords: Crystal Structure Prediction (CSP); USPEX algoritm; Trivalent dinitrides; CaO-SiO_2 polymorphism

Different properties of materials can now be computed with high accuracy from quantum mechanical calculations even on commodity computers. Density functional theory (DFT) and related approximations have become the workhorse methods in chemistry, solid-physics and materials science, but also in other fields as geology. In the last decades, it has also emerged the importance of including thermal effects in DFT calculations for better quality predicted properties. Usually, a harmonic approximation (HA) is adopted but for some physical quantities and phenomena anharmonic effects must be included. In this respect, the quasi-harmonic approximation (QHA) offers an effective approach to go beyond HA by letting the vibrational frequencies depend on volume. The availability in different codes of suitable computational tools to calculate the vibrational properties of solids [Baroni et al. 2001, Pascale et al. 2004] makes it possible to routinely combine the QHA with DFT. Here, I will discuss the application of the QHA methodology as implemented in the CRYSTAL program [Erba A. 2014, Dovesi et al. 2018] to the study of soft materials such as molecular crystals and porous solids. Firstly, the thermal expansion and thermodynamic functions, and quasi-static approximation for anisotropic thermoelasticity of crystal urea [Erba et al. 2016] will be presented. Results will be shown to reliably describe thermal properties thorough a comparison with experimental data. Secondly, I will focus on the investigation of the combined effect of temperature and pressure on the structural and mechanical properties of a prototypical metal-organic framework material: MOF-5 [Ryder et al. 2019]. The softening upon compression of low-energy phonon modes at the ? point reveals a symmetry-reducing group-subgroup phase transition that has a significant effect on the nature of the mechanical response. The negative thermal expansion of the porous material is also nicely reproduced.

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Viscosity of olivine, plagioclase, and chromite crystal-mushes and implications for compaction-driven fluid flow

James A. D. Connolly, Max W. Schmidt

ETH Zurich, Department of Earth Sciences, Zurich, Switzerland

Keywords: Crystal mushes; Centrifuging experiments; Carman-Kozeny porosity-permeability

Centrifuging experiments on olivine, chromite, and plagioclase in the presence of basaltic liquid show evidence of viscous compaction. The compaction profiles are inconsistent with the porosity-dependence ascribed to the viscosity in macroscopic compaction models. This inconsistency is eliminated by adopting the porosity-dependence derived from microscopic models for a matrix that compacts by grain-boundary diffusion-controlled creep. The time to halve the porosity of natural olivine igneous sediments by compaction is estimated from the centrifuging experiments to be $O(10^3)$y. Half-times for plagioclase and chromite layers are substantially longer $O(10^4$-$10^5)$y, suggesting that such layers only compact if they have been loaded by additional sedimentation. At conditions relevant to melt flow in asthenospheric settings and trans-crustal magmatic systems, the bulk and shear viscosities inferred for olivine and plagioclase are $O(10^{17})$Pa·s and imply time- and length-scales for viscous compaction that are substantially shorter than previously anticipated. Our analysis serendipitously reveals that the often neglected quadratic solidity term of the Carman-Kozeny porosity-permeability relation is essential to prevent non-physical behavior in models of cumulate sedimentation.

Gas-grain Interactions in for the Origin of Water in Earth the Solar Nebula and Implications

Jibamitra Ganguly[1], Abu Aasaduzzaman[2]

[1]*University of Arizona, Department of Geosciences, Tucson, Arizona, USA*
[2]*Pennsylvania State University, School of Science, Engineering and Technology, Harrisburg, Pennsylvania, USA*

Keywords: Origin of water; Solar Nebula; Chemisorption

The origin of water in Earth, which constitutes a fundamental problem in the Earth and Planetary Sciences as well Astrobiology, has been a highly debated issue. The currently popular models invoke its delivery by chondritic meteorite type materials [Piani et al., 2020; Marty, 2012]. In this work we discuss some limitations of these models and, expanding our earlier work [Asaduzzaman et al., 2015], explore the potential of delivery of water into the earth via dissociative chemical adsorption on mineral grains, primarily olivine, within the nebular environment, using a combination of thermodynamic and quantum chemical calculations. It is found that at least a few ocean-equivalent of water (OEW) could have incorporated into the earth via chemisorption; the associated D/H fractionation, calculated according to [Asaduzzaman and Ganguly, 2021], causes deuterium enrichment in the chemisorbed water relative to the solar nebula (SN), increasing with decreasing temperature and leading to the observed enrichment factor of ~ 4 at ~ 300 K. There does not seem to be any kinetic impediment to equilibration at such low temperature. Calculations for benzylic and aromatic hydrocarbons in the insoluble organic matter of primitive carbonaceous chondrites [Remusat et al., 2006] suggest that the observed deuterium enrichment in these organics might have been due to equilibrium fractionation with the solar nebula at ~175-200 K. Estimates of terrestrial water budget range from 3-7 OEW [Marty, 2012] and even higher. Our calculations suggest that at least a significant portion of this water was derived directly from the SN itself via chemisorption; however, contributions from other sources and mechanisms were also likely to have taken place. We emphasize that since chemisorption was unavoidable, its contribution must be considered in the models of the origin of water in Earth. We predict that the D/H ratio of water or hydroxyls within the earth's interior should be variable and may differ from that of ocean water that has been used to constrain the bulk D/H ratio of terrestrial water.

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Real space approaches to chemical bonding and physical properties

Carlo Gatti

Istituto di Scienze e Tecnologie Chimiche (SCITEC), consiglio Nazionale delle Ricerche (CNR), Milano, Italia

Keywords: Schrödinger's equation; Probabilistic interpretation; Quantum Chemical Topological

With increasing number of electrons *N*, the amount of information stored in a wavefunction Ψ soon escapes human comprehension and information compression techniques need to be so adopted. Two main paths are followed for this purpose [Martín Pendás and Gatti, 2021]. The first, exploits the models used to solve Schrödinger's equation in order to rationalize Ψ. One-electron orbital based descriptions are thus customarily used, since the knowledge and manipulation of *N* 3D functions is much easier than that of Ψ. Yet, this simplification comes at the expense of several problems. Orbitals are not unique, due to the infinite number of their transformations that leave the total Ψ invariant, and are also largely method dependent. The second adopted path compresses the information contained in Ψ using its probabilistic interpretation. It leads to the extraction from Ψ of real space functions, such as the electron density (ED), the pair ED, the electrostatic potential (EP), which are then analysed using the tools of topology, giving rise to the Quantum Chemical Topological (QCT) approaches and to a vast number of physically unbiased descriptors to discuss chemical bonding and the ensuing system's or material's properties [Saleh et al., 2019]. Thanks to my QCT expertise and the codes I developed for implementing QCT also for solids, I had in my life the privilege to be contacted by eminent mineralogists or geochemists, like G.V. Gibbs, A. Oganov and G. Ottonello, for studies on silicates and on exotic systems under high pressure. After discussing the QCT tools used in such studies, recent QCT progresses on the decomposition of the EP in suitable moieties contributions [Gatti et al., 2020] and on the relationship between chemical bonding in chalcogenides phase change materials and their peculiar properties will be presented [Raty et al., 2019]. Though applied to different research areas, these QCT progresses may perhaps be of potential interest also for geochemical applications.

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Towards an *ab initio* physically-consistent thermodynamic dataset for deep mantle phases: the case of Mg_2SiO_4 ringwoodite

Mattia La Fortezza[1], Francesca Menescardi[1], Donato Belmonte[1,2]

[1] *Università degli Studi di Genova, Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Genova, Italia*

[2] *Museo Nazionale dell'Antartide, Sezione di Genova, Italia*

Keywords: *Ab initio* DFT-B3LYP calculations; Mg_2SiO_4 ringwoodite; Ambient and HP-HT conditions

A major shortcoming of current thermodynamic databases for phase equilibrium calculations at deep mantle conditions is the lack of comprehensive and physically-consistent thermodynamic data of the constituent mineral phases. Thermodynamic assessments are calibrated over the results of selected HT-HP experiments, which may suffer from uncertainties related to technical problems, metastability issues or the unquenchable nature of some mantle minerals. This may lead in turn to assessed thermodynamic properties for mantle phases which may be internally-consistent but clearly suffer from physical unsoundness, thus hindering a close link between thermodynamic modelling, seismological observations and mantle dynamics. In that sense, ab initio calculations based on quantum-mechanical theory are one of the most reliable methods available to obtain information on thermodynamics, phase relations and seismic properties of deep Earth minerals. In this work we performed *ab initio* DFT-B3LYP calculations to determine thermodynamic properties of Mg_2SiO_4 ringwoodite, the stable polymorph of olivine in the lowermost mantle transition zone (~520-660 km depths). Thermodynamic properties of ringwoodite have been computed in the framework of quasi-harmonic approximation by full phonon dispersion calculations, which allow to accurately reproduce the vibrational density of states both at ambient and HP-HT conditions. Computed thermal expansivity and thermoelastic properties supports the evidence that QHA performs remarkably well for ringwoodite up to mantle transition zone temperatures. Since volume thermal expansion of ringwoodite is strongly pressure-dependent and its pressure dependence becomes more marked with the increasing temperature, internally-consistent assessments and empirical extrapolation of thermoelastic data to deep mantle conditions should be taken with care to avoid inaccurate or spurious predictions in phase equilibrium and mantle convection numerical modelling.

Modelling fluid-mediated redox processes with micro-inclusions

Nadia Malaspina

Università degli Studi di Milano-Bicocca, Dipartimento di Scienze dell'Ambiente e della Terra, Milano, Italia

Keywords: Redox processes; Slab-mantle interface; Maowu Ultramafic Complex (China)

The redox processes taking place at the slab-mantle interface are poorly investigated and the redox potential of slab-derived fluid phases is still poorly constrained. The subducted oceanic lithosphere contains considerable amounts of iron so that the Fe^{3+}/Fe^{2+} equilibria in mineral assemblages can buffer the (intensive) fO$_2$. Alternatively, Fe^{3+}-bearing fluids can be carrier of (extensive) 'excess oxygen' when transferred from the slab to the mantle, prompting the oxidation of the sub-arc mantle. Therefore, the correct use of intensive and extensive variables to define the slab-to-mantle oxidation by slab fluids is of primary importance when considering different fluid/rock ratios. Garnet orthopyroxenites from the Maowu Ultramafic Complex (China) derive from harzburgite precursors that reacted with silica-rich liquids at 4 GPa, 750-800 °C, representing a proxy of supra-subduction mantle affected by metasomatism from crust-derived fluid phases. This metasomatism produced orthopyroxene and garnet rich of solid multiphase inclusions filled by epitactic spinel, hydrous minerals and liquid water, derived from trapped solute-rich aqueous fluids. To investigate the redox budget of these fluid phases, the Fe^{3+} of inclusions infillings were measured with TEM-EELS. Forward modelling fO$_2$ calculations indicate that the garnet orthopyroxenites record ?FMQ = -1.8 / -1.5, resulting more reduced than metasomatised supra-subduction peridotites. On the other hand, oxygen mass balance, performed both on the Maowu hybrid orthopyroxenite and on metasomatised supra-subduction garnet peridotites, indicate that the excess of oxygen (nO$_2$) is the same (10 mol m^{-3}). The oxygen mass balance of the crust-derived fluids also indicates that the fluid precipitates are more oxidised than the host rock, reaching up to 400 mol m^{-3} of nO$_2$. This suggests that slab fluid phases could be potentially carrier of oxidised components when they escape the slab-mantle interface.

Molecular dynamics strategies to determine the melting curve of CaO

Francesca Menescardi[1], Davide Ceresoli[2] and Donato Belmonte[3]

[1]*Università di Genova, Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Genova, Italia*
[2]*Istituto di Scienze e Tecnologie Chimiche (SCITEC), Consiglio Nazionale delle Ricerche (CNR), Milano, Italia*
[3]*Museo Nazionale dell'Antartide, Sezione di Genova, Italia*

Keywords: *Ab initio* molecular dynamics; CaO melting curve; Void-nucleated method – Z-method

The thermodynamic properties of multicomponent liquids at high pressure and temperature (HP-HT) are of paramount importance to elucidate the melting and crystallization phase relations in geological systems. High-pressure melting experiments suffer from uncertainties of hundreds of K and rarely predict the ultimate nature of melting [Belmonte et al., 2017]. Ab initio molecular dynamics (AIMD) gave useful insights on the structure-energy properties of solid and liquid phases up to very HP-HT conditions, but the calculated melting temperature (T_m) depends critically on the simulation protocol and on the number of atoms to process. In this work we focus on the melting curve of CaO, not only because is a key phase in material and geological sciences, but also because the thermodynamic properties of the liquid phase are still controversial due to the very high melting point of the crystal [Sun et al., 2010; Alvares et al., 2020]. The simplicity of its phase diagram makes it a good candidate for AIMD simulations. However, AIMD simulations are expensive, while classic MD with empirical potentials allows to employ different strategies at a very low computational cost. We simulate the melting process of CaO with classic molecular dynamics, by the means of the LAMMPS code. We tested three different methods. The two-phase method [Zykova-Timan et al., 2005] consists of running a solid-liquid interface at constant enthalpy. The melting temperature is determined as the average equilibrium temperature. The void-nucleated method [Alvares et al., 2020] exploits holes in the crystal structure to initiate the melting process, thus decreasing the unrealistic high melting point resulting from homogeneous heating simulations. Conversely, the Z-method [Belonoshko et al., 2006] exploits homogenous melting, but the actual melting temperature is obtained as the average temperature in a constant energy run, provided that the initial configuration is sufficiently over-heated.

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Iron oxidation state in the Earth's lower mantle

Marcello Merli[1], Costanza Bonadiman[2], Alessandro Pavese[3]

[1]*Università di Palermo, Dipartimento di Scienze della Terra e del Mare, Italia*
[2]*Università di Ferrara, Dipartimento di Fisica e Scienze della Terra, Italia*
[3]*Università di Torino, Dipartimento di Scienze della Terra, Italia*

Keywords: Earth lower mantle; Oxidation state of iron; Prediction model

The nature of the Earth's interior redox conditions is a function of the redox sensitive elements incorporated therein at our planet's formation (in particular: ferrous, ferric and native Fe). Therefore, the oxidation state of iron plays a central role in affecting the geochemical and geodynamic evolution of the Earth and its atmosphere, and in this light, it is motivating investigations and attracting attention [Sinmyo et al, 2017]. Oxidation state of an element at extreme regimes i) is expected to possibly change with respect to room conditions, ii) depends on the crystal-chemical structure of the phase hosting the species under investigation and iii) requires a principle to ascribe electrons to a given atom. We developed a model to predict Fe oxidation state at LM-conditions under the following hypotheses: i) iron that may lead to Fe^{3+} occupies twelvefold coordination sites of bridgmanite, the latter assumed to have a reference composition of $(Mg_{0.75}Fe_{0.25})SiO_3$ associated with Fe^{2+}; ii) the Bader [Bader, 1990] theory was used to model the electronic basin ascribable to a given atom, so as to calculate thereby the electrons that do belong to the species whose oxidation state we aim to predict; iii) some atomic replacement reactions were considered to promote Fe oxidation at different degrees and weighted one against another to take account of their contributions, the latter estimated by the reaction occurrence probability and involved chemical species abundance; iv) Fe partitioning between Fe-periclase and bridgmanite is taken from Merli et al [2017]. In doing so, we developed a model that predicts ferric ion up to 20-30% in the earth lower mantle.

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Thermodynamic properties of quartz from *ab initio* calculations: the role of anharmonicity

Mara Murri[1] and Mauro Prencipe[2]

[1]*Università di Milano-Bicocca, Dipartimento di Scienze dell'Ambiente e della Terra, Italia*
[2]*Università di Torino, Dipartimento di Scienze della Terra, Italia*

Keywords: *Ab initio* calculations; Quarzt – Anharmonicity

The simple chemistry and structure of quartz together with its abundance in nature and its piezoelectric properties allow us to employ it for several applications: from engineering to Earth sciences. For these purposes, the quartz equations of state and its thermoelastic and thermodynamic properties have been studied since decades [e.g., Carpenter et al., 1998; Scheidl et al., 2016]. Alpha quartz is stable up to 2.5 GPa at room temperature [e.g., Bose and Ganguly, 1995] where it converts to coesite, and at ambient pressure up to 847 K [e.g., Carpenter et al., 1998] where it transforms to the beta phase. In particular, since the displacive phase transition at 847 K at ambient pressure is driven by intrinsic anharmonicity effects (soft-mode phase transition), its precise mechanism is difficult to be investigated experimentally. Therefore, we performed ab initio calculations in the framework of the statistical thermodynamics approach to study these anharmonic effects. We determined the principal thermodynamic quantities accounting for the intrinsic anharmonicity and we compared them against experimental data. Our results up to 700 K show a very good agreement with experiments. The same procedures and algorithms reported here can also be applied to determine the thermodynamic properties of other crystalline phases possibly affected by intrinsic anharmonic effects, that could partially invalidate the standard quasi-harmonic approach.

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Thermodynamics of jeffbenite ($Mg_3Al_2Si_3O_{12}$) from *ab initio* calculations

Mauro Prencipe[1], Donato Belmonte[2], Fabrizio Nestola[3]

[1]*Università di Torino, Dipartimento di Scienze della Terra, Italia*
[2]*Università di Genova, Dipartimento di Scienze della Terra, dell'Ambiente e della Vita, Italia*
[3]*Università di Padova, Dipartimento di Geoscienze, Italia*

Keywords: *Ab initio* calculations; Jeffbenite, Perple_X program

Jeffbenite ($Mg_3Al_2Si_3O_{12}$), previously known as TAPP: tetragonal-almandine-pyrope-phase, space group $I\text{-}4_2d$, has been found as inclusion in diamonds from São Luiz river, Juina district of Mato Grosso, Brazil [Nestola et al., 2016]. Since the diamonds from that locality are presumed to originate at large depths in the Earth mantle (*super-deep diamonds*), and since jeffbenite is recovered only in that kind of diamonds, jeffbenite was considered a phase stable at higher pressures compared to those limiting the stability fields of the supposedly *parent* pyrope or majorite phases. With the aim to constraint the stability field of jeffbenite (thus providing information concerning the depth within the Earth mantle where it was trapped in diamonds) a thermodynamic modeling has been attempted. However, concerning this phase, no thermodynamic parameters were available in literature, so that they were computed from *first principles*, at the hybrid Hartree-Fock/Density functional Theory (HF/DFT) level, within the limit of the quasi-harmonic approximation and in the framework of statistical thermodynamics. In particular, equation of state (bulk modulus at standard conditions, its first derivative with respect to pressure, and its temperature dependence), thermal expansion, specific heat and their temperature dependence, and the entropy at standard conditions were computed. The Gibbs free energy at standard conditions (G_0), in the appropriate scale, was computed from the difference of the *ab initio* energy of jeffbenite with respect to pyrope, also estimated at the same *ab initio* level as jeffbenite, and rescaled to the G_0's found in the thermodynamic databases used for subsequent computations [Holland and Powell, 2011; Stixrude and Lithgow-Bertelloni, 2005].

The Perple_X program [Connolly, 2005] was then used to compute pseudosections for fixed global stoichiometries of the system corresponding to several significant mineral assemblages. In all of the tested cases, jeffbenite resulted to be less stable than pyrope at high pressures and temperatures; in particular, jeffbenite was never predicted to be stable with respect to pyrope at pressure exceeding 6 GPa at low temperature (600K), and dropping to about 2 GPa at 1200K. If confirmed, such results will require a new interpretation concerning the significance of finding jeffbenite in super-deep diamonds.

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Cation speciation and redox state in silicate glasses: Insights from low-temperature calorimetry

Pascal Richet

Institut de Physique du Globe de Paris, Paris, France

Keywords: Silicate glasses; Low-temperature heat capacity; Boroxol rings; Iron-bearing silicates

Silicate glasses have such a fundamental and practical importance that understanding of the relationships between their composition, properties and structure is needed. In this respect, the low-temperature heat capacity (C_p) is a valuable as it is a sensitive probe of short- and medium-range order around cations. This is illustrated here by insights yielded on the varying speciation exhibited by aluminum and boron and the existence of several redox states for iron. For calcium aluminosilicate glasses, composition independent partial molar C_ps and entropies have been determined for SiO_2, CaO and three different kinds of Al_2O_3 in which Al is 4-, 5- and 6-fold coordinated by oxygen. Hence, short-range-order around Si and Ca does not depend on aluminum speciation up to the highest ^{V}Al fractions studied. Because of the higher $S298$ - $S0$ of $^{IV}Al_2O_3$ (72.8 J/mol K) compared with $^{V}Al_2O_3$ (48.5 J/mol K), the partial molar configurational C_p of Al_2O_3 in melts includes a negative contribution associated with temperature-induced changes from ^{IV}Al to ^{V}Al. For sodium borosilicates, partial molar C_ps and vibrational entropies are derived in a similar way from 15 to 300 K with B_2O_3 components where boron is 3- or 4-fold coordinated. The $S298$ - $S0$ of 70 and 35 J/mol K obtained for $^{III}B_2O_3$ and $^{IV}B_2O_3$, respectively, illustrate the major role of boron speciation on the vibrational density of states. The strong influence of boroxol rings on these properties is also apparent. For iron-bearing silicates, an analysis for samples based on sodium disilicate and calcium Tschermak molecule compositions yield $S298$ - $S0$ values of 56.7 and 116 J/mol for FeO and Fe_2O_3, respectively Association with $^{IV}Fe^{3+}$ for charge compensation does not entail changes in coordination for both Ca^{2+} and Na^{+}. At very low temperatures, however, C_p additivity breaks down because of specificities in medium-range order closely related to the boson peak, which is much stronger for reduced than for the oxidized glasses.

SESSION 2 - ENVIRONMENTAL GEOCHEMISTRY

Conveners:
Carmine Apollaro (Università della Calabria), Rosa Cidu (Università degli Studi di Cagliari), Elisa Sacchi (Università degli Studi di Pavia)

Figure caption: View of the Priolo petrochemical plant (Sicily). Photo by Sergio Calabrese

Priority environment and health risk. The thallium case-history

Riccardo Petrini

Università di Pisa, Dipartimento di Scienze della Terra, Italia

Keywords: Thallium-contaminated waters, Acidic waters; Pietrasanta (central Italy)

Despite environmental factors are the root cause of a significant disease burden, the different legalistic regulations seem to obscure the connection between environment and human health. Thallium is one of the most toxic trace metals, listed by both the US-EPA and EU as a dangerous pollutant. The European COST Action TD1407 included Tl in the list of Technology-Critical Elements, which are key components for the development of new technologies with associated increasing environmental impact and potential threats. Thallium is also considered a priority pollutant in both the 12th and 13th five-year plans in China. Although highly toxic, until recently Tl remained an obscure element compared to its neighbours, lead, mercury and cadmium. Indeed, thallium is not requested to be mandatorily surveyed for the quality of water intended for human consumption. Because of the lack of obligations for chemical testing, it is possible that Tl-contaminated springs, in particular settings, may be used in the distribution systems inducing health negative effects that may remain undiscovered for long. This poses challenges for regulatory Agencies. Thallium is released by both anthropogenic and geogenic sources; in particular, Tl can be greatly enriched in some sulfides or even act as a mineral-forming element, and may be introduced into local environments by industrial operations and in mine settings. In soil, Tl reacts with other constituents and its fate depends on a number of factors. The research presented here focuses on the severe thallium contamination discovered in northern Tuscany Region (Pietrasanta municipality) where the worldwide highest Tl levels were detected in strongly acidic waters in abandoned mine settings. Thallium-contaminated underground waters jeopardize the quality of potable water used by local communities. The results obtained during a five-year multidisciplinary study are discussed, highlighting the link between geochemistry and health.

Deep Antarctic ice as a geochemical reactor: Terrestrial and Martian implications

Giovanni Baccolo[1,2], Barbara Delmonte[1], Paul B. Niles[3], Giannantonio Cibin[4], Elena Di Stefano[1,2], Massimo Frezzotti[5], Dariush Hampai[6], Yoshinori Iizuka[7], Lindsay Keller[3], Valter Maggi[1,2], Augusto Marcelli[6,8], Joe Michalski[9], Christoph Snead[10]

[1]*Università Milano-Bicocca, Dipartimento di Scienze Ambientali, Italia*
[2]*Istituto Nazionale di Fisica Nucleare, Sezione di Milano-Bicocca, Italia*
[3]*NASA Johnson Space Center, USA*
[4]*Diamond Light Source, Harwell Science and Innovation Campus, UK*
[5]*Università di Roma Tre, Dipartimento di Scienze, Italia*
[6]*Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali di Frascati, Roma, Italia*
[7]*Hokkaido University, Institute of Low Temperature Science, Japan*
[8]*Rome International Center for Materials Science, Italia*
[9]*University of Hong Kong, Department of Earth Sciences, Hong Kong*
[10]*Jacobs, NASA Johnson Space Center, USA*

Keywords: Antarctic ice; Mineral dust; Synchrotron radiation X-ray absorption spectroscopy

Mineral dust in Antarctic ice has been extensively used as a proxy for paleoclimatic reconstructions. This has been possible because minerals in deep ice have always been considered relatively stable. Our recent studies show that this assumption is not always valid. The deep englacial environment can act as a geochemical reactor, favoring the dissolution and precipitation of specific minerals. We present data gathered from the analysis of dust samples from a deep Antarctic ice core drilled at Talos Dome (East Antarctica). The ice core is 1620 m long and its age at 1548 m deep is 343 ka. We analyzed Fe-mineralogy and -speciation in dust samples extracted from the ice core by means of synchrotron radiation X-ray absorption spectroscopy. Results show that the distribution of Fe-minerals with depth present trends related to ice-depth and -age. In particular we highlight the first englacial identification of jarosite. This iron(III)-potassium hydrated sulphate is not present in the first 1000 m of the ice core, but below this depth its concentrations progressively increases, until becoming the most dominant Fe-bearing mineral in the last 100 meters of the core. Concurrently, the concentration of other Fe(II)-minerals decreases with depth, such as hornblende, pyrite, muscovite. This evidence suggests that in the deep part of the Talos Dome ice core, mineral dust undergoes to wet oxidative-acidic weathering. This is supported by the englacial precipitation of jarosite, which requires an acidic brine to form, by the oxidative trend of Fe over depth, and by the dissolution of ferrous minerals. Our finding has important implications which range from ice core paleoclimatology to Martian geochemistry. The englacial precipitation of jarosite supports the ice-weathering model proposed to explain the formation of jarosite on Mars, highlighting the importance of ice-related geochemical reactions with respect to Mars surficial mineralogy.

Two-year monitoring of water hydrochemistry in a Pb-Zn Mississippi Valley-Type mine (MVT) in the Southeastern Alps (Raibl, Friuli Venezia Giulia)

Nicolò Barago[1], Elena Pavoni[1], Federico Floreani[1], Matteo Crosera[2], Gianpiero Adami[2], Davide Lenaz[1], Stefano Covelli[1]

[1]*Università degli Studi di Trieste, Dipartimento di Matematica e Geoscienze, Italia*
[2]*Università degli Studi di Trieste, Dipartimento di Scienze Chimiche e Farmaceutiche, Italia*

Keywords: Pb-Zn Mississippi Valley-Type; Decommissioned mining site; Hydrogeochemistry; Raibl mine (northern Italy)

The recent and past mining activities are among the main anthropic sources of dispersion of potentially toxic trace elements (PTEs) in the environment. In this study, a two-year monitoring of different water bodies in a decommissioned mining site located in the Southeastern Alps (Friuli Venezia Giulia, Raibl mine) was performed. Results have allowed to provide a characterisation of the hydrogeochemistry, the chemical signatures and the temporal-spatial variations of PTEs in a carbonate-hosted Pb-Zn Mississippi Valley-Type (MVT) mine, where no acid mine drainages (AMD) occur. Besides mineralogy and pH-Eh conditions, strong rainfalls and high-flow events are the main factors affecting the temporal variability of dissolved PTEs, promoting their dissolution and dispersion. Anomalous concentrations of trace metals (Zn, Pb, Tl) were found in near neutral pH-buffered groundwaters entrapped in tailings impoundments, whereas concentrations of metalloids (As, Sb and Ge) were more abundant in low-flow water drainage from mine adits. High concentrations of Tl were found in the saturated area of the tailings impoundments, related to relatively lower pH and sulfate ions contents, thus suggesting Tl-bearing pyrite/marcasite oxidation. At the same time, low concentrations of dissolved Ge and Cd in groundwaters entrapped in tailings are possibly associated to sphalerite-depleted post-flotation tailings. Based on chemical data, modeling and literature, attenuation processes of dissolved PTEs (mainly Pb) are mainly attributed to sorption onto Fe-oxy-hydroxides, which is pH-dependent, and precipitation of mineral phases (e.g., dissolved Zn to hydrozincite: $Zn_5(CO_3)_2(OH)_6$). The Tl/Zn and Tl/Pb ratios show that enrichments occur without notable attenuation inside the tailings impoundments, possibly indicating that Tl attenuation needs higher pH to effectively promote adsorption onto Fe-oxy-hydroxides [Coup and Swedlund, 2015], as, conversely, occurs in the Rio del Lago stream waters.

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Impact on air quality of carbon and sulfur volatile compounds emitted from hydrothermal discharges: the case study of Pisciarelli (Campi Flegrei, South Italy)

Rebecca Biagi[1], Franco Tassi[1,2], Stefano Caliro[3], Francesco Capecchiacci[1,3], Stefania Venturi[1,2]

[1]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Italia*

[2]*Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia*

[3]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano, Italia*

Keywords: Air pollutants; Hydrothermal emissions; Pisciarelli (Campi Flegrei, southern Italy)

Volcanoes are to be regarded as natural sources of air pollutants. Climatic and environmental forcing of large volcanic eruptions are well known, although species emitted during periods of quiescence or hydrothermal activity can also be highly impactful. Based on compositional and isotopic data, a survey on the spatial distribution in air of CO_2, CH_4, H_2S and SO_2 emitted from the fumarolic field of Pisciarelli (Campi Flegrei, South Italy), a hydrothermal area where degassing activity has significantly increased since 2009, was carried out. The aims of this study were (i) to assess the impact on air quality of these natural manifestations and (ii) inquire into the behavior of the selected species once released in air, and their possible use as tracers to distinguish natural and anthropogenic pollutant sources. Keeling plot analysis of CO_2 and CH_4 isotopes revealed that the hydrothermal area acts as a net source of CO_2 in air, whilst CH_4 originated mainly from anthropogenic activities. Approaching the urban area, anthropogenic CO_2 sources increased and, at distances greater than 800 m from the Pisciarelli field, they prevailed over the hydrothermal signal. While hydrothermal CO_2 simply mixed with that in the atmospheric background, hydrothermal H_2S was affected by oxidation processes. Accordingly, SO_2 generated by oxidation of hydrothermal H_2S was recognized in the air near the hydrothermal emissions, whereas anthropogenic SO_2 was measured at the measurement sites located within the urban area. Noteworthy, in the proximity of a geothermal well, whose drilling was in progress during our field campaign, the H_2S concentrations have reached values up to 3 orders of magnitude higher than the urban background, claiming the attention of the local authorities.

Distinguishing sources of nitrate in groundwater

Riccardo Biddau[1], Stefania Da Pelo[1], Luca Marcia[1], Mario Lorrai[2], Maurizio Testa[3], Elisabetta Dore[1], Paolo Botti[2], Rosa Cidu[1]

[1]Università degli Studi di Cagliari, Dipartimento di Scienze Chimiche e Geologiche, Italia
[2]Regione Sardegna, Cagliari, Italia
[3]Agenzia Regionale per la Protezione dell'Ambiente della Sardegna, Cagliari, Italia

Keywords: Hydrogeochemistry; Nitrate pollution; Sardinia

Anthropogenic inputs have significantly impacted the nitrogen cycle, with NO_3^- pollution being a major concern affecting water resources worldwide [Shukla and Saxena, 2019]. The EU Nitrates Directive [EC, 1991] aimed to protect water quality by preventing and reversing degradation of groundwater due to NO_3^- from agricultural, urban and industrial wastes; NO_3^- concentrations should not exceed the limit of 50 mg/L in water bodies. Therefore, assessing NO_3^- sources is a fundamental prerequisite for planning sustainable groundwater management. In Sardinia, according to the EC Nitrates Directive, the intensively farmed area of Arborea was designated as Nitrate Vulnerable Zone [R.A.S., 2005]. In 2011, a program aimed at groundwater quality monitoring started. The NO_3^- concentration in groundwater varied from <0.8 to 515 mg/L and median 19 mg/L; 23% of values were higher than 50 mg/L. Flat and hilly areas in eastern Sardinia were the zones mostly affected by NO_3^- contamination. To estimate potential NO_3^- sources, groundwater samples were collected at 174 sites from 2013 to 2019. Hydrogeochemistry, stable isotopes (D, O, N, S and B), statistics (Gaussian mixture and Bayesian isotope mixing models) and land uses were combined to assess NO_3^- sources. The use of manure was a primary contributor to NO_3^- pollution, whereas urban sewage and synthetic fertilizers were subordinated. Results of this study have been used by the Sardinian Regional Authorities to review critical areas, giving a relevant contribution in identifying the new vulnerable zones according to the Nitrate Directive.

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Imaging the 2D trace elements distribution in polar ice cores to assess the preservation of the paleoclimate record

Pascal Bohleber[1], Marco Roman[1], Nicolas Stoll[2], Piers Larkman[1], Barbara Stenni[1], Barbara Delmonte[3,4] and Carlo Barbante[1]

[1]*Università Ca' Foscari Venezia, Dipartimento di Scienze Ambientali, Informatica e Statistica, Italia*

[2]*Alfred-Wegener-Institut Helmholtz-Zentrum für Polar- und Meeresforschung, Bremerhaven, Deutschland*

[3]*Università degli Studi di Milano-Bicocca, Dipartimento di Scienze dell'Ambiente e della Terra, Italia*

[4]*EUROCOLD Laboratory for Glaciology and Paleoclimate, Milano, Italia*

Keywords: Polar ice cores; 2D trace elements distribution; Antarctica

Deep polar ice cores are a cornerstone of modern paleoclimate research, archiving a unique variety of proxies, including aerosol-related atmospheric impurities, over timescales from decades to hundreds of millennia [Fischer et al., 2021]. To decipher the deepest and thus oldest part of the ice core impurity record, it is key to employ high-resolution analysis of the most highly thinned layers. At this fine scale, understanding the interaction of impurities with the ice crystal matrix becomes essential to avoid misinterpretation. Being a high spatial resolution, high sensitivity and micro-destructive technique, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has unique potential in this regard, especially since it was recently refined for state-of-the-art 2D impurity imaging [Bohleber et al. 2020]. We apply our method for high-resolution chemical imaging analysis of impurities in polar ice cores samples. This reveals that many impurities are preferentially located in the interstitial volumes between adjacent crystals, the so-called "grain boundaries". We show how the task to disentangle the grain boundary imprint from the stratigraphic layer signal may have broad impacts on the interpretation of LA-ICP-MS signals from deep ice [Bohleber et al., 2021]. Furthermore, we explore the implications of our findings for investigating post-depositional layer changes, in particular regarding known processes such as grain growth and deformation [Stoll et al., 2021], impurity diffusion [Ng, 2021] and chemical reactions [Baccolo et al., 2021]. With this, we aim at fully exploiting the potential of LA-ICP-MS imaging for assessing record preservation in a future 1.5 million year "Oldest Ice Core" from Antarctica.

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Tracing vertical distribution of NAPL contaminations: two case studies

Alessandra Briganti[1], Martina Mattia[2], Mario Voltaggio[1], Paola Tuccimei[2],
Michele Soligo[2], Elisa Rainaldi[3]

[1]Istituto di Geologia Ambientale e Geoingegneria (IGAG), Consiglio Nazionale delle Ricerche (CNR), Montelibretti, Italia
[2]Università Roma Tre, Dipartimento di Scienze, Italia
[3]Mares s.r.l., Italia

Keywords: NAPL contamination; Radon; Pump stations; Rome (central Italy)

Radon deficit technique was applied to study the vertical distribution of the local Non-Aqueous Phase Liquid (NAPL) contamination in two different sites, in Rome. The higher solubility of ^{222}Rn in NAPLs than in water or air is well-known and already used to localize the spatial distribution of a NAPL plume [De Miguel et al., 2020; Schubert, 2015]. In two pump stations Rn deficit was periodically measured in groundwater to monitor the areal distribution of NAPL [Briganti et al. 2021; Mattia et al. 2020]. The first site is characterized by a shallow aquifer and the vertical Rn distribution was determined by inserting 12 passive accumulators at different depths in two different wells. These PDMS-AC (polydimethylsiloxane and activated carbon) accumulators selectively absorb ^{222}Rn and they are impermeable to groundwater and humidity occurring in the wells [Voltaggio & Spadoni, 2013]. After reaching equilibrium in two weeks, the Rn accumulated by PDMS-AC was counted using high resolution ?-spectrometry. The second site is characterized by volcanic deposits with a groundwater level about at -18 meters and equipped with a soil venting system. After purging, this equipment was used to sample soil gas at different intervals of depth from 1 to 18 m. Rn values were determined by Durridge RAD7. The method was optimized to collect and analyze the gas directly. A parallel test was performed to measure Rn content by PDMS-AC method at the same levels. Preliminary data indicates the possible application of the two methods to assess vertical distribution of NAPL contaminant, considering local geological setting. Main differences are related to the kind of produced data (a relative value integrated in time or an instantaneous absolute value) and dependence on infrastructural equipment. Determining vertical Rn distribution, either in groundwater or in soil gas, generates a clear impact on remediation of NAPLs pollutions and a better reconstruction of the plume and of the pollutant.

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Major and trace elements characterization of atmospheric deposition in volcanic, urban and industrial areas of Sicily (Italy): preliminary results

Filippo Brugnone[1], Walter D'Alessandro[2], Francesco Parello[1], Filippo Saiano[3], Maddalena Pennisi[4], Marcello Liotta[2], Sergio Bellomo[2], Lorenzo Brusca[2], Anna Maria Abita[5], Lorenza Li Vigni[1], Sergio Calabrese[1,2]

[1]Università degli Studi di Palermo, Dipartimento di Scienze della Terra e del Mare, Italia
[2]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italia
[3]Università degli Studi di Palermo, Dipartimento di Scienze Agrarie, Alimentari e Forestali, Italia
[4]Istituto delle Geoscienze e delle Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Pisa, Italia
[5]Agenzia Regionale per la Protezione dell'Ambiente (ARPA-Sicilia), Palermo, Italia

Keywords: Atmospheric deposition; Technology-critical elements; Sicily (southern Italy)

The source of chemical elements dissolved in rainwater can be both natural and anthropogenic. A group of trace elements has been recently brought to attention for their possible environmental impacts, the Technology-critical elements (TCEs). The current knowledge about the geochemical cycle of TCEs is still scarce, nevertheless recent studies [e.g., Brugnone et al., 2020] evidenced a contribution from the volcanic activity for some of them (Te, Tl, and REE). Our research aims to produce a geochemical database on major and trace element depositions in different areas of Sicily: a volcanic area (Etna), two urban areas (Palermo, Catania), two industrial areas (Milazzo, Priolo), and a rural monitoring site (Cesarò). The samples are collected monthly through a network of 15 bulk collectors. Here we report about the chemical composition of rainwater from the first five sampling campaigns. The pH was between 5.5 and 7.8, with an average value of 7.0. EC showed values ranging from 8 to 184 µS/cm, with an average of 72 µS/cm. The most abundant major elements were Cl^- and SO_4^{2-} for anions, Ca^+ and Na^+ for cations. Regarding trace elements, the highest volume-weighted mean (VWM) concentrations were generally measured in the areas affected by volcanic emissions, especially for TCEs, such as Te and Tl, which show VWM concentrations of 4.5 ng/L and 50.8 ng/L, respectively, higher than the VWM values detected in samples far from the volcanic source (0.8 ng/L and 2.5 ng/L, respectively). Exceptions are Zn and Br with the highest VWM concentration found in the Priolo area, Cr and Fe in Palermo. The contribution of the various sources, including the volcanic one, can therefore be well evidenced through the characterization of the chemical composition of the atmospheric deposition.

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The UAV (Unmanned Aerial Vehicle) - Lumex® combination as a new tool to investigate the 3D distribution of GEM (Gaseous Elemental Mercury) in the lower atmosphere in near real-time

Jacopo Cabassi[1], Marta Lazzaroni[1,2], Luciano Giannini[1], David Mariottini[3], Barbara Nisi[1], Daniele Rappuoli[4,5], Orlando Vaselli[1,2]

[1]Istituto delle Geoscienze e delle Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia
[2]Università di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia
[3]Drone Arezzo S.r.l., Arezzo, Italia
[4]Unione dei Comuni Amiata Val d'Orcia, Unità di Bonifica, Piancastagnaio, Siena, Italia
[5]Parco Museo Minerario di Abbadia San Salvatore, Abbadia San Salvatore, Siena, Italia

Keywords: Gaseous Elemental Mercury; Unmanned Aerial Vehicle; Abbadia San Salvatore (central Italy)

Proposing new measurement methods for gaseous mercury is becoming crucial to monitor the presence and the behavior of mercury pollution sources and enforce the knowledge on mercury dispersion mechanisms to the atmosphere according to the provisions of the Minamata Convention on Mercury. Within this framework, we present the first attempt to couple a Lumex® RA-915M and an UAV (Unmanned Aerial Vehicle, a heavy-lift octocopter) to directly and continuously measure GEM (Gaseous Elemental Mercury) in the lower atmosphere. The effectiveness of the UAV-Lumex® combination was tested at different heights in selected sites pertaining to both mining facilities of the former Hg-mining area of Abbadia San Salvatore (Mt. Amiata, Italy), known as a GEM source, and surrounding urban zones. The combination allowed to shed light on the GEM concentration variability and to depict the GEM distribution in the atmosphere up to 60 m above the ground, thanks to the Lumex® great sensitivity and the octocopter directional versatility, which could be stopped at selected altitudes. The acquisition system optimization consisted of: i) Lumex® and UAV GPS data synchronization by means of a stand-alone GPS, ii) a vertical sampling tube connected to the Lumex® inlet to overcome the rotors strong airflows and iii) batteries for power supply to avoid the release of exhaust gases. The resulting dot-map graphical representations provided a realistic 3D picture of GEM profiling during the flights in near real-time, useful to check whether the guideline concentrations were exceeded. The data acquisition accuracy and the experience of the UAV pilot allowed to standardize the flights, i.e. accurately repeating the flight paths in different times by reprogramming the route based on previously acquired data. The results showed that the GEM concentrations in the urban area remained at relatively low values, whilst displayed significant variations and higher values above some mining facilities.

An appraisal on methane emissions from wetlands based on direct estimates and theoretical computations: the case of Lake Porta wetland, northern Tuscany (Italy)

Gioia Capelli Ghioldi[1], Franco Tassi[1,2], Stefania Venturi[1,2], Francesco Capecchiacci[1,2,3], Orlando Vaselli[1,2], Marta Lazzaroni[1], Barbara Vietina[4]

[1]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Italia*

[2]*Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia*

[3]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano, Italia*

[4]*Comune di Montignoso, Ufficio Ambiente, Massa Carrara, Italia*

Keywords: Wetlands; CH_4 fluxes; Lake Porta (central Italy)

Methane (CH_4) emissions to the atmosphere are a rising concern affecting the Earth's climate. Among natural sources, wetlands contribute to 30% of global CH_4 emissions, making flux assessment from these environments pivotal. Any attempt to establish a theoretical estimate of gas flux from aquatic ecosystems should address the rate of gas exchange between the air-water interface, a process commonly modelled as driven by two variables: the difference in gas concentration between water and air and the gas transfer velocity (k). The magnitude of gas exchange, thus the value of k, has been shown to be related to wind speed, a parameter through which k is calculable. In this study, diffusive CH_4 fluxes were measured at Lake Porta, a coastal wetland in northern Tuscany (Italy), adopting the floating static chamber (FSC) method. Two field campaigns were carried out in March and July 2021 to evaluate the influence of seasonal variations. As the measured data showed that significant amounts of CH_4 are emitted into the air, the fluxes were compared with those obtained from theoretical computations based on empirical relationships from literature where k values were achieved experimentally. The results show coherent trends in the measured and calculated fluxes, with a regular shift related to the assumptions the authors made in determining the k coefficient. This study offers a methodologic approach on both empiric and theoretical estimates of greenhouse gas fluxes from aquatic ecosystems, which may be critical for future climate change scenarios.

Historical trends of Pb pollution in the metropolitan area of Milano

Davide De Giorgi[1], Vincenzo Gargano[1], Cinzia Rossiello[1], Chiara Compostella[1], Elena Ferrari[1], Gianluca Sessa[1], Cristina Colombi[2], Eleonora Cuccia[2], Umberto Dal Santo[2], Massimo Tiepolo[1]

[1]*Università degli Studi di Milano, Dipartimento di Scienze della Terra, Italia*

[2]*Agenzia Regionale per la Protezione dell'Ambiente (ARPA-Lombardia), Settore Monitoraggi Ambientali, Qualità dell'Aria, Milano, Italia*

Keywords: Pb pollution; Dendrochemistry; Soil analysis; Milan (northern Italy)

Trends of air pollution for Pb in metropolitan areas are usually limited to few decades. However, a long-range view is essential to constrain sources and the effectiveness of the actions undertaken to contain pollution. The metropolitan area of Milano underwent a very rapid development after WWII with rapid growth of population, vehicular traffic, and industrial activities with the side effect of introducing toxic metals, and Pb in particular, into the environment. In recent years traffic restrictions (e.g., AREA C) were imposed to buffer and reduce air pollution. Here we reconstructed the historical trends of Pb pollution after WWII by combining dendrochemistry and soil analysis. Tree cores from both *Ulmus and Quercus* species, with associated soils, were sampled in the metropolitan area of Milano at different distances from the city-center. Tree rings were analyzed with laser ablation ICP-MS and soils were digested in aqua regia prior analysis by ICP-MS. Pb concentrations in tree cores (either *Ulmus* or *Quercus* species) from the city center of Milano are historically lower (up to 10 times) than those in the more external sampled areas. The two tree species however show different Pb trends likely related to a different local exposure. An *Ulmus* tree core from Città Studi area has returned the longest historical record (more than 70 years) and its location close to an ARPA air monitoring station allowed a crosscheck of results since 2005. Here, Pb concentrations show an abrupt enrichment after WWII, a steady decrease after the mid-50s and then a new increase during mid 70s with a maximum in the mid-90s. After this period a steady decrease begins, likely related to the unleaded gasoline introduction, and only in 2020 Pb levels are comparable with those of the mid-70s. Noticeably, the close agreement between dendrochemical Pb trends and those from air monitoring stations supports the reliability of this approach to air pollution.

Soil and groundwater background values at abandoned mining areas of Sardinia

Roberto Dessì[1], Fabio Carta[3], Rosa Cidu[4], Giovanni De Giudici[4], Martina Demurtas[3], Michela Ebau[4], Enrico Mantega[1], Alessandro Murgia[2], Patrizia Olla[2], Maurizio Testa[1], Gabriele Uras[3], Paolo Valera[3]

[1]*Agenzia Regionale per la Protezione dell'Ambiente (ARPAS-Sardegna), Cagliari, Italia*

[2]*Regione Autonoma della Sardegna, Dipartimento della Difesa Ambientale, Cagliari, Italia*

[3]*Università di Cagliari, Dipartimento di Ingegneria Civile, Ambientale e Architettura, Italia*

[4]*Università di Cagliari, Dipartimento Scienze Chimiche e Geologiche, Italia*

Keywords: Abandoned mine sites; Waters and Soils; Virtual Cloud; Sardinia

Mining activity in Sardinia left 151 abandoned mine sites, which constitute important sources of metals and metalloids contamination. ARPAS was commissioned by the Regional Authority of Sardinia to lead the project "Determination of the background values in the soils and groundwater of abandoned mine areas", carried in partnership with the University of Cagliari. The reference for the background assessment is the "Guidelines for the determination of background values for soils and groundwater" [SNPA, 2018]. The large number of mine sites, their characteristics and the widespread occurrences of mineralization, may result in concentrations of metals and metalloids of environmental concern. These features require an approach for the background values assessment different with respect to that normally used at small sites. Therefore, a specific conceptual model and appropriate clustering of data in homogeneous area was developed. For the processing of such a big data, consisting of more than 100k records and several thematic geo mining layers, a virtual Cloud framework area was developed. This Cloud allows the partners to interact each other, exchange and elaborate data. Historical data is currently collected in the Cloud and a GeoDatabase has been created using open-source software. To calculate the background of soils and groundwater it was decided to cluster the mine sites in metallogenic districts, based on a robust conceptual model. The database was mainly developed by the collection, validation and systematization of historical data collected by mining companies. The project plans the collection and analyses of about 1000 soil samples and 500 groundwater samples around the mine sites. The final target of the project is to publish a Background Atlas aimed to spread it via web, to the public stakeholders involved in the reclamation of abandoned mine areas.

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Sources and dispersion of antimony at the abandoned mine of Su Suergiu (SE Sardinia)

Elisabetta Dore, Riccardo Biddau, Dario Fancello, Daniela Medas, Stefano Naitza, Nicola Rigonat, Giovanni De Giudici, Rosa Cidu

Università degli Studi di Cagliari, Dipartimento di Scienze Chimiche e Geologiche, Italia

Keywords: Sb pollution; Waters; Su Suergiu (SE Sardinia)

Antimony (Sb) pollution linked to present and past mining activities is a current environmental concern. Typical Sb concentrations in natural unpolluted waters are less than 1 µg/L, but can increase up to 10^3-10^4 µg/L near mining and smelting sites. This study investigates the processes involved in the Sb release and dispersion in the abandoned Sb mine area of Su Suergiu (SE Sardinia). For this purpose, mineralogical (XRPD) and minero-chemical (SEM-EDS) analyses have been performed on outcropping rocks, mine wastes and foundry slags; moreover, the Sb contents in waters draining the mine area and surroundings have been determined. Waters flowing at Su Suergiu show slightly alkaline pH and oxidizing conditions, and their chemical composition is Ca(Na)-sulfate. Waters of adits, spring and streams sampled in the mine area show variable Sb content, between 48 and 4,020 µg/L (median: 323 µg/L). The drainage waters collected downstream the foundry slag heaps reaches 10^4 µg/L of Sb concentration, indicating that the residues of Sb metallurgy, especially metallic Sb and Sb_2O_3 (valentinite/sénarmontite) dumped in the foundry slag heaps, are the main Sb pollution sources at Su Suergiu. Of particular interest is the presence of mopungite, $NaSb(OH)_6$, that acts as a temporary, highly soluble sink for Sb. Waters draining the mine area flow into the Riu Ciurixedda stream, which in turn flows into the Flumendosa River, a major regional source of water for agricultural and domestic uses. After the Riu Ciurixedda confluence, the Sb concentration in the Flumendosa waters increases above drinking water limits set by the World Health Organization (20 µg/L) and European Community (5 µg/L). Results show that Sb(V), stable under oxidizing conditions as dissolved $Sb(OH)_6^-$ in a wide range of pH, prevails over the less mobile Sb(III) in the studied waters, explaining Sb dispersion up to several kilometers downstream the mine area, where natural Sb attenuation occurred mainly by dilution.

Assessing baseline concentrations of aqueous contaminants at abandoned mines

Michela Ebau[1], Fabio Carta[2], Giada Floris[1], Elisabetta Dore[1], Riccardo Biddau[1], Giovanni De Giudici[1], Roberto Dessì[3], Maurizio Testa[3], Gabriele Uras[2], Rosa Cidu[1]

[1]*Università degli Studi di Cagliari, Dipartimento di Scienze Chimiche e Geologiche, Italia*

[2]*Università degli Studi di Cagliari, Dipartimento di Ingegneria Civile, Ambientale e Architettura, Italia*

[3]*Agenzia Regionale per la Protezione dell'Ambiente della Sardegna (ARPAS), Cagliari, Italia*

Keywords: Aqueous contaminant; Arsenic; Furtei (Sardinia)

This work, funded by the Regional Authority of Sardinia and leaded by ARPAS, aims to evaluate the baseline values of groundwater at Sardinian former mines, according to the Italian guidelines [SNPA, 2018]. Tertiary andesite-hosted epithermal gold deposits were exploited at Furtei (Sardinia) from 1997 to 2003. Propylitic, argillic, advanced argillic and silicification alterations with increasing sulphide contents were recognized [Ruggieri, 1997]. Weathering of abundant pyrite and enargite generated acid drainages, metal and metalloid contaminants in the water system. At present, the former mine is under environmental remediation. Monitoring of dissolved contaminants at 28 piezometer sites was established in 2016, resulting in a dataset comprising 376 samples. In the 2020 survey the dataset was implemented by the determination of major components, hydrogen and oxygen isotopic signatures. Water samples were distinguished into two subsets: WARP contains the waters interacting with the weakly altered rocks; DARP contains those interacting with deep altered rocks. Different approaches were used for the evaluation of baseline values. The dataset was first processed excluding the potentially contaminated waters; then, dataset processing included all waters and those outliers consistent with hydrogeochemical criteria. The latter approach ensured a greater reliability considering the geological and geochemical context, so it has been chosen for the calculation of baseline values. The 95%USL (upper limit of the maximum value) was adopted and a range of values proposed. Lower values correspond to WARP 95%USL and higher values to DARP 95%USL (e.g. As baseline was 46 µg/L, much higher than limits established for drinking water).

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Gaseous mercury evasion from bare and grass-covered contaminated soils at the Isonzo River alluvial plain (North Eastern Italy)

Federico Floreani[1,2], Valeria Zappella[1], Alessandro Acquavita[3], Jadran Faganeli[4], Stefano Covelli[1]

[1]*Università degli Studi di Trieste, Dipartimento di Matematica e Geoscienze, Italia*
[2]*Università degli Studi di Trieste, Dipartimento di Scienze della Vita, Italia*
[3]*Agenzia Regionale per la Protezione Ambientale del Friuli Venezia Giulia (ARPA- FVG), Udine, Italia*
[4]*National Institute of Biology, Marine Biology Station, Piran, Slovenia.*

Keywords: Gaseous elemental mercury; Soils; Isonzo River alluvial plain (north-eastern Italy)

Emissions of gaseous elemental mercury (Hg^0) from soil surface represent a relevant component of the global biogeochemical cycle of this element. Terrestrial environments characterised by a high mercury (Hg) content in the substrate due to natural enrichments and/or anthropogenic activities may be an important source of Hg^0 for the atmosphere [Eckley et al., 2016]. The alluvial plain of the Isonzo River (NE Italy) suffered a significant contamination due to the historical extraction of the cinnabar ore from the upstream Idrija mine (Slovenia). The magnitude and extension of Hg contamination of soils in this area have been recently described in detail [Acquavita et al., 2021], although an assessment of Hg^0 releases from the soil is still lacking. In this work, Hg^0 evasion fluxes at the soil-air interface were measured by means of a non-steady state flux chamber coupled with a real-time Hg^0 analyzer (Lumex RA-915M) at 6 sites within the Italian sector of the Isonzo plain in summer. At each site, distinct sets of measurements were performed at regular time intervals during the diurnal period, both on bare and grass-covered soils, together with monitoring of soil and air temperature and incoming UV radiation. Moreover, soil samples were analyzed for organic matter content and total Hg concentration. Gaseous Hg fluxes (range=48.2÷944.6 ng m^{-2} h^{-1}) were comparable with values reported for other sites impacted by mining activity worldwide [Agnan et al., 2016] and generally resulted 1.5- to 3-times higher for bare than grass-covered soils at each site, confirming the role of vegetation cover in influencing Hg release to the atmosphere. Overall, the amount of Hg^0 fluxes at different sites seems to be related to total Hg content of soils (range=1.98÷28.93 mg kg^{-1}), although the correlation was significant only for bare soils. Finally, Hg^0 fluxes were found to track the incoming UV radiation during sampling, likely due to Hg photo-reduction on surface and soil heating.

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The potential mercury remobilization from soil and biomass in the Mt. Amiata mining district (Italy) during a wildfire

Silvia Fornasaro[1], Giovanni Delicato[2], Francesco Ciani[2], Guia Morelli[3], Pilario Costagliola[2], Valentina Rimondi[2], Pierfranco Lattanzi[3], Marco Fioravanti[4]

[1]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italia*

[2]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Italia*

[3]*Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia*

[4]*Università degli Studi di Firenze, Dipartimento di Agraria, Italia*

Keywords: Mercury remobilization; Wildfires; Mt. Amiata (central Italy)

About the 10% of global mercury (Hg) emissions to the atmosphere are due to biomass burning during a wildfire. We calculated the release of Hg by a hypothetical wildfire at two sites (Abbadia San Salvatore, ABS and Vivo d'Orcia, VO) in the Monte Amiata Mining District (MAMD), southern Tuscany (Italy), where past Hg mining affects local Hg concentrations. The two sites are located at 1.5 km (ABS) and 3 km (VO) from the mining area. The biomass components of black pine (*Pinus nigra* Arn.) and chestnut (*Castanea sativa* Mill), among the most frequent species in the MAMD, were sampled in a woodland area of 630 m^2 (VO) and 1066 m^2 (ABS). Bark (n=25), wood (n=18), and pine needle (n=3) were collected in February 2020. Chestnut leaves were not collected due to winter sampling. At each site, topsoils (= litterfall, first 7 cm) and subsoils (7-15 cm) were collected below the trees (n=22). Hg was measured by means of a direct Hg analyzer (DMA). We quantified: i) the Hg content in plant biomass and soil; ii) the involved biomass at each site (allometric equations); iii) the mass of Hg stored in each site. To estimate Hg emissions during a hypothetical wildfire we assumed that: i) barks and needles release 100% Hg (complete burning); ii) only 20% of wood is combusted; ii) topsoil burning releases 100% of Hg; iii) subsoil does not contribute to Hg emissions. At both sites, Hg concentrations vary in the order soil>bark>needles>wood and were higher in pine trees. The calculated Hg storages (tree components + soil) are 1375 g/ha at ABS and 321 g/ha at VO. The topsoil is the major reservoir for Hg (>90-95%). Among biomass, wood is the major reservoir (56%) followed by barks (42%), and lastly needle (2%). These findings should be included in the implementation of existing fire management and prevention activities. Climate change scenario, with the increasing occurrence of wildfires might result in spikes of Hg concentrations in the atmosphere, possibly near to human sensitive sites.

Inducing pH-controlled formation of LDH for removal of divalent metals from circum-neutral drainage from mining wastes

Franco Frau[1], Alfredo Idini[2], Roberta Atzori[3], Daniela Medas[1], Francesca Podda[1], Elisabetta Dore[1], Gioacchino Tempesta[4], Giovanna Agrosì[4]

[1] *Università degli Studi di Cagliari, Dipartimento di Scienze Chimiche e Geologiche, Italia*
[2] *Via Salvino Naitana 5, 07100, Sassari, Italia*
[3] *Via Giuseppe di Vittorio 9, 09010, Fluminimaggiore (SU), Italia*
[4] *Università degli Studi di Bari "Aldo Moro", Dipartimento di Scienze della Terra e Geoambientali, Italia*

Keywords: Mining wastes; Heavy metals; Layered double hydroxide (LDH)

The neutral M^{2+}-rich and M^{3+}-poor (M = metal) drainage from a mining waste dump in SW Sardinia (Italy) was used to test the removal of metals through the precipitation of layered double hydroxide (LDH) induced by adding Al^{3+} (a metal missing in the drainage) and maintaining or bringing back the pH to a circum-neutral value [Frau et al., 2020]. The main parameter controlling the removal of metals and the type of precipitate was the pH. As a function of pH variation during the experiments, analyses of precipitates and solutions showed either the formation of poor crystalline LDH combined with very high removal of Zn, Ni and Pb (92-100%), more variable removal of Mn (46-98%) and less Cd (33-40%), or the formation of more crystalline LDH combined with lower removal of Zn (62%), Mn (43%), Ni (88%), Pb (64%) and especially Cd (1%). The different metal removal efficiency is clearly affected by the following factors: 1) the two pH steps of the method; 2) the direction of pH variation within each step. In particular, the highest removal of metals is obtained when the first pH step goes towards acidic conditions, as a consequence of Al salt addition, and precipitation of an amorphous hydrated hydroxysulfate of Al (probably a precursor of felsöbányaite $Al_4(SO_4)(OH)_{10}·4H_2O$) occurs. This first acidic pH step removes little or no metals (just 0-3%) but it is essential so that the second pH step towards slightly alkaline conditions, as a consequence of NaOH addition, can be highly efficient in removing divalent metals as the amorphous hydrated hydroxysulfate of Al gradually turns into an LDH incorporating Zn, Mg and other metals. On the contrary, when both pH steps are maintained in the neutral-alkaline range, a more crystalline LDH forms and a lower metal removal is observed. These results encourage further investigations on the removal of metals by inducing LDH precipitation at different pH conditions as a simple and effective method for polluted drainage water treatment.

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Evaluating the Performance of Statistical Indices to Explore Macroscale Geochemical Evolution of Watersheds

Caterina Gozzi, Antonella Buccianti and Orlando Vaselli

Università di Firenze, Dipartimento di Scienze della Terra, Italia

Keywords: Compositional Data Analysis; Watersheds; Environmental monitoring

Watersheds exhibit a wide heterogeneity of landscape properties and complex responses to varying climatic and anthropogenic inputs. Assessing the potential of new statistical indices in tracing the geochemical evolution of watersheds is of great importance to seek emergent features and properties governing their behavior. This work focuses on comparing three statistical indices under the Compositional Data Analysis theory [Aitchison, 1982] able to capture the geochemical evolution of a composition: i) the cumulative sum of unclosed perturbation factors of each composition (row sum) with respect to a pristine reference, ii) the robust Mahalanobis distance, describing the compositional differences from the same reference and, iii) the geometric mean of the composition as a measure keeping record of the interactions among the constituents. The indices are calculated for water and stream sediment composition of the Tiber River (central Italy) to test their different performance [Gozzi and Buccianti, 2021]. The results highlight source-to-sink compositional changes, allowing to understand how geochemical footprints propagate downstream. All indices provide consistent results, especially if high-variability species are treated separately and low values are rare. Under this latter condition, the geometric mean of the composition shows a high correlation with the cumulative sum of unclosed perturbation factors. This indicates that both measures inherit the complex history of the changes, well capturing the inner workings of the system under the influence of external drivers. The application of these methods for environmental monitoring and applied geochemical studies will facilitate the extrapolation of generalizable macroscale laws, enabling an enhanced prediction of watersheds behavior across different areas.

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Helicrysum italicum (roth) G. Don, a promising species for the phytostabilization of polluted mine sites: a case study in the Montevecchio mine (Sardinia, Italy)

Nicolas Greggio, Alessandro Buscaroli, Denis Zannoni, Enrico Dinelli

Università Alma Mater Studiorum di Bologna, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Unità Operativa di Ravenna CIRSA, Ravenna, Italia

Keywords: Phytoremediation properties; Potentially Harmful Elements; Polluted mine soils

Mine exploitations worldwide generated a great amount of tailings still containing huge quantities of Potentially Harmful Elements (PHEs) that are spread out in the environment. This study aims at assessing the phytoremediation properties of *Helicrysum italicum (roth) G. Don*, and in particular the capacity to absorb, transfer and accumulate Cd, Cu, Ni, Pb and Zn, in the plant tissues. A restricted literature review (7 papers) is also proposed in order to verify *H. italicum* use in phytoremediation strategy of polluted mine soils. A number of 22 contaminated sites from Montevecchio mine area (Sardinia, Italy) are sampled and compared with 6 uncontaminated sites. In each site both rhizospheric soil materials and *H. italicum* plants are sampled. Total composition by XRF, and bioavailable fractions by DTPA-extraction, are analysed on soil samples. *H. italicum* roots, stems and leaves are separately analysed to extract PHEs from the different plant parts. Results show that Cd and Zn are the most bioavailable PHEs in contaminated sites, while Cd, Cu, Pb and Zn exceed the thresholds of the Italian environmental legislation. *H. italicum* plants growing on contaminated soils statistically accumulate more Cd, Ni, Pb and Zn than plants grown on uncontaminated soils, while no significant differences are found for Cu concentrations. The root/soil ratios are >1 in both sites meaning that *H. italicum* can be defined as a tolerant species useful for remediation of metal-polluted soils. The leaf/root ratios weakly >1 of Zn, Pb and Cu and <1 of Ni and Cd indicate *H. italicum* not suitable for phytoextraction. Our results are aligned with the available literature indicating *H. italicum* a tolerant species especially for Cd, Pb and Zn. The low leaf/root ratios along with its being a spontaneous and perennial species able to propagate seeds directly on contaminated soils recommended the use of *H. italicum* as pioneering strategy for the phytostabilization.

Mineralogical and geochemical studies and application of octacalcium phosphate as precursor of fluorapatite for water defluoridation

Alfredo Idini[1], Franco Frau[2], Giorgio Ghiglieri[2,†]

[1]*Via Salvino Naitana 5, 07100, Sassari, Italia*
[2]*Università degli Studi di Cagliari, Dipartimento di Scienze Chimiche e Geologiche, Italia*
[†]*passed away*

Keywords: Water defluoridation; Octacalcium phosphate (OCP); Tanzania

The consumption of water with fluoride (F^-) concentration higher than 1.5 mg/L (WHO recommended limit for drinking water) is recognized to cause serious diseases, and F^- removal from naturally contaminated waters is a health priority for more than 200 million people worldwide [Yadav et al., 2018]. The octacalcium phosphate (OCP), a mineralogical precursor of bio-apatite, was tested as F^- remover and the removal experiments were performed in batch-mode using different initial concentrations of F^- (from 40 to 140 mg/L) and different reaction times. The results show that the experimental F^- removal capacity of OCP is 25.7 mg/g, and 4 g of OCP can effectively treat 1 L of water with F^- concentration up to 50 times higher than the drinking limit [Idini et al., 2019]. XRD and chemical characterization of the solid phases indicate that OCP transforms into fluorapatite (FAP) uptaking F^- from solution. The property of OCP to be the crystalline precursor of apatite has been also investigated using equal molar amounts of fluoride, chloride, hydroxyl, and carbonate anions, to assess if and how the anionic competition can influence the formation of the different apatite end-members. The investigation shows that F^- is the main anion removed from solution during the OCP reaction, and consequently FAP is the main resulting apatitic phase, followed by hydroxyapatite [Idini and Frau, 2021]. With the aim of carrying out a field trial, an innovative household-scale device based on the application of OCP has been developed. The defluoridator prototype essentially consists of a 20 L tank and a recirculating pump that guarantees the interaction between water and OCP. The results of tests performed in rural areas of Tanzania show that a standardized dose of OCP (4 g for 2 hours of working time) can lower dissolved F^- from an initial concentration of 21 mg/L to less than the WHO drinking limit of 1.5 mg/L without secondary adverse effects on water quality [Idini et al., 2020].

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Heavy metals contamination in surface waters and suspended solid loads from the Nievole River Valley sub-basin (Tuscany, Central Italy)

Chiara Maccelli[1,2], Claudio Natali[2], Barbara Nisi[3], Martina Casalini[2],
Orlando Vaselli[2,3], Stefania Venturi[2], Riccardo Avanzinelli[2]

[1]Università di Pisa, Dipartimento di Scienze della Terra, Italia

[2]Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Italia

[3]Istituto delle Geoscienze e delle Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia

Keywords: River geochemistry; Radiogenic isotopes; Nievole River Valley (central Italy)

The Nievole River Valley (NRV) is a sub-basin of the Arno River Basin, located in Tuscany (Central Italy) and characterised by a complex riverine network in its northern part, since it hosts the Nievole, Pescia di Collodi, and Pescia di Pescia rivers, and several other artificial channels that crosscut the basin and collects effluents from many small cities and industrial districts. All these rivers and channels inflow into the Padule di Fucecchio, a crucial swampy zone for the migratory routes of several bird species, whose waters are only regulated by the Usciana River. The study area insists within a complex ecosystem characterised by relevant anthropic activities and small-medium enterprises, such as paper mill industries, flora farms, thermal spas, and one of the most productive Italian tanning districts, thus representing an ideal case study for the identification of natural and anthropogenic contributions to the geochemical composition of environmental matrices. In this work, a preliminary evaluation of the NRV river system quality is presented by analysing water and suspended solid load (SSL) samples collected in 2021 along the main courses and tributaries, distributed in an area of about 320 km^2. The preliminary data highlighted a wide geochemical spectrum of the investigated waters, also dependent by seasonal variations, which ranged from $Ca^{2+}(Mg^{2+})$-HCO_3^- to Na^+-$Cl^-(SO_4^{2-})$ geochemical facies. The most relevant variations, for the high and low river discharge periods, were pertaining to the N-bearing species, which varied from 36 to 80 (NO_3^-), from 2.4 to 1.2 (NO_2^-), and from 12 to 23 (NH_4^+) mg/L. Interestingly, relatively high Cs concentrations, from 37 to 170 µg/L in the waters over the period of sampling and up to 46 ppm in the SSLs only regarding the high river discharge period, were recorded. SSLs produced Pb isotopic signatures typically associated with the presence of anthropogenic contributions, which were more evident in those samples collected from the most urbanized and industrialized areas.

The chemical speciation of phosphatic fertilizers in the context of the new European Regulation 2019/1009

Maria Chiara Manghi[1], Elisabetta Peruzzi[2], Riccardo Calzavara[2], Pier Luigi Graziano[2], Bruno Pavoni[1], Mauro Masiol[1]

[1]*Università Ca' Foscari Venezia, Dipartimento di Scienze Ambientali, Informatica e Statistica, Italia*
[2]*Arvan s.r.l., Venezia, Italia*

Keywords: Phosphatic fertilizers; Elemental analyses; EU Fertilizing Products and Amending Regulation 2019/1009

The EU Fertilizing Products and Amending Regulation 2019/1009 will introduce limit values for Cd, Cr, Pb, Hg, Ni and As in phosphatic fertilizers. The Directive will enter into force in 2022 with an initial limit value for Cd of 60 $mg_{Cd}kg_{P2O5}^{-1}$, progressively lowered to 40 $mg_{Cd}kg_{P2O5}^{-1}$ by 2025 and to 20 $mg_{Cd}kg_{P2O5}^{-1}$ by 2034. This is the most stringent regulation in the World and its outcomes might penalize the phosphorite export from ore deposits with high Cd concentrations. In particular, the regulation could make the Western European production of phosphatic fertilizers unsustainable, by restricting the phosphatic rocks supply [Ulrich, 2019], e.g., from North Africa, where most of the phosphorite for the European market is extracted. Up today, there are no datasets comprehensively representing the chemical composition of fertilizers in Europe. The present research has analyzed 41 fertilizers from the Italian market, including diammonium phosphates, simple and triple superphosphates, NPK, organo-mineral fertilizers as well as raw phosphorites. Samples were pulverized and microwave acid digested. Elemental analyses were performed in ICP-OES (Na, Mg, Al, Si, P, S, K, Ca, Fe, Se, Hg) and ICP-MS (Li, Be, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Cd, Sn, Sb, Ba, Tl, Pb, Bi, U). Specific methods were tested to optimize the dissolution of different matrices against standard reference materials NIST SRM-695 and BCR-032. The first results show that all samples comply with the new standards for As, Ni, Pb and Cr. For Cd (range 0.06-120 $mg_{Cd}kg_{P2O5}^{-1}$) almost all analyzed fertilizers will comply with the initial limit value, but the percentage decreases to 75% and to 50%, when considering the future more stringent limit values. This situation will inevitably cause significant impacts on the sector.

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Particulate matter pollution across the Veneto Region, a European hotspot for air quality: 15 years of studies

Mauro Masiol[1], Gianni Formenton[2], Flavia Visin[1], Stefania Squizzato[1], Elena Innocente[2], Elisa Danesin[1], Maria Chiara Manghi[1], Agnese Abbadessa[1], Francesco Menegon[1]

[1]Università Ca' Foscari Venezia, Dip. Scienze Ambientali, Informatica e Statistica, Italia
[2]Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto (ARPAV), Dipartimento Regionale Laboratori, Venezia Mestre, Italia

Keywords: Particulate matter pollution; Source and origin of PM; Veneto (northern Italy)

The Po Valley is one of the few remaining European hotspots for air pollution. A peculiar topography favors air mass stagnation over a densely anthropized territory with complex emission scenarios, leading to the buildup of particulate matter (PM) pollution. The Veneto Region lies in the eastern part of the Po Valley, the side open to the Adriatic Sea. Thus, its air pollution phenomenology is complicated by coastal atmospheric circulation patterns and potential transboundary transport of polluted air masses. This contribution aims to summarize the main results of several research programs carried out over the past 15 years [e.g., Masiol et al., 2021; Formenton et al., 2021] by discussing: (i) the general improvement of air quality in the last decades due to the implementation of European air quality management policies, increasingly stringent standards, and economic drivers; (ii) the factors, origin, and sources affecting the PM concentration and its geochemical composition; (iii) the quantification of the main potential sources of PM pollution; (iv) the changes in emission scenarios producing changes in the PM composition and in the geochemical fingerprints of sources; and (v) next challenges due to the increase of biomass burning emissions for domestic heating.

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Study of underground cavities using total gamma radiation mapping: case studies in Roma (Italy)

Martina Mattia[1], Paola Tuccimei[1], Michele Soligo[1], Manuela Portaro[1],
Fabio Bellatreccia[1], Letizia Rustico[2]

[1]*Università degli Studi Roma Tre, Dipartimento di Scienze, Italia*
[2]*Soprintendenza Speciale Archeologia Belle Arti e Paesaggio di Roma, Italia*

Keywords: Total gamma radiation measurement; Underground cavities; Rome (central Italy)

Natural radioactivity is a spontaneous process due to the instability of the nuclides which change through a process of decay releasing ionizing radiation which may consist of particles or particularly energetic electromagnetic waves, the gamma rays. Gamma radiation from the ground is mainly due to gamma-emitting radionuclides in the ^{238}U, ^{235}U and ^{232}Th decay series. Moreover, 40K also strongly contributes to gamma radiation, especially in Roma and surrounding areas, where K-rich ignimbrites from Colli Albani and Sabatini volcanoes crop out. Previous work [Di Paolo et al., 2013; Lucchetti et al., 2019] showed that the signal obtained from total gamma radiation measurements depends on certain parameters such as lithology, which influences the abundance of radionuclides present, the topographic setting and sinkholes occurrence. In fact, it has been seen that where there are gaps or underground cavities, the resulting radiation signals are lower due to the lack of volume of rock. The purpose of the present work is therefore to verify the effectiveness and validity of the total gamma radiation measurement technique for the identification and the study of underground cavities in different study sites in Rome. Field surveys were carried out using a gamma spectrometer with a sodium iodide crystal. The scintillator is connected to a digital ratemeter equipped with a built-in scaler that provides timed counts over a user-specified period. Several grids of measuring points were established to map gamma radiation. Total gamma activity expressed as counts per second (CPS), was processed and mapped with Surfer® (Golden Software), a contouring and analysis software.

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Molecular-scale geo-bio interactions in the rhizosphere-plant system of *Juncus acutus* exposed to different Zn sources

Daniela Medas[1], Carlo Meneghini[2], Claudia Pusceddu[1], Ilaria Carlomagno[3], Giuliana Aquilanti[3], Elisabetta Dore[1], Vittorio Murgia[4], Francesca Podda[1], Valentina Rimondi[5,6], Salvatore Vacca[1], Richard B. Wanty[7], Giovanni De Giudici[1]

[1]Università di Cagliari, Dipartimento di Scienze Chimiche e Geologiche, Italia
[2]Università degli Studi Roma Tre, Dipartimento di Scienze, Italia
[3]Elettra-Sincrotrone Trieste, Basovizza, Italia
[4]Soc. Agr. Sgaravatti Land Cons. Arl, Cagliari, Italia
[5]Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Italia
[6]Istituto delle Geoscienze e delle Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia
[7]Colorado School of Mines, Golden, USA

Keywords: Trace metals; Rhizosphere-plant system; *Juncus acutus*

Trace metals (Zn, Fe, Pb, etc.) occur in the environment due to both natural and anthropogenic processes. Understanding the interactions between metals and plants is a fundamental issue we must face because metals released into the environment will inevitably interact with plants, which are basic components of ecosystems. Moreover, revealing metal mobilization/immobilization processes at the molecular level is fundamental to developing remediation strategies such as phytoremediation.

In this study, we investigated the molecular-scale processes controlling the Zn pathway in the rhizosphere-plant system of *Juncus acutus*, combining chemical, X-ray diffraction and X-ray absorption near edge structure analysis. Specifically, rhizobox experiments were conducted, under greenhouse conditions, employing three growing substrates, characterised by different Zn contents (140, 9700 and 20400 mg/kg), and two irrigation lines with low (0.05 mg/l) and high (180 mg/l) Zn contents in water. Zinc accumulation and distribution in *J. acutus* tissues is affected by the Zn content in the substrate and in the water. *J. acutus* accumulates Zn mainly in roots (up to 10000 mg/kg dry weight) and its translocation increases as the Zn content in the substrate decreases. Also, Zn chemical speciation is affected by Zn exposure, resulting in different complexation mechanisms. These are, mainly, driven by cysteine and citrate compounds whose amount, in the rhizosphere and in the vegetal tissues, increases when Zn content in water is high. This study presents the role played by the rhizosphere minerals and by the water composition on the Zn geo-bio transformations, revealing that *J. acutus* can lead to variable Zn pathways when Zn is additionally supplied by watering, and pointing out the huge complexity of the rhizosphere-plant interactions.

Distribution of Hg, As and Sb in soils and stream sediments from Abbadia San Salvatore and surrounding areas (Mt. Amiata, southern Tuscany, Italy)

Federica Meloni[1,2], Orlando Vaselli[1,2,3], Barbara Nisi[2,3], Francesco Bianchi[4], Daniele Rappuoli[5,6]

[1] *Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia*
[2] *Interuniversity Consortium - INSTM, Firenze, Italia*
[3] *Istituto delle Geoscienze e delle Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia*
[4] *S.B.C. Geologi Associati, Firenze, Italia*
[5] *Unione dei Comuni Amiata Val d'Orcia, Unità di Bonifica, Piancastagnaio, Siena, Italia*
[6] *Parco Museo Minerario di Abbadia San Salvatore, Abbadia San Salvatore, Siena, Italia*

Keywords: Soil and stream sediment geochemistry; Mercury; Mt. Amiata (central Italy)

The distribution of Hg, As, and Sb in top- and sub-soils and stream sediments from the area of Abbadia San Salvatore and surroundings (eastern flank of the Mt. Amiata volcano, southern Tuscany, Italy) was defined. The Mt. Amiata mining area has been the 4th largest district in the world for the production of mercury by exploiting HgS. Here, the mining activity started at the end of the 18th century, and it shut down at the end of 1970. The geology of the study area is dominated by volcanic rocks (mainly trachydacites and to a lesser extent rhyodacites and olivine-latites) and calcareous argillaceous rocks belonging to the Ligurian Units. In this work, 44 top-soils (10-40 cm), 44 sub-soils (50-140 cm), and 20 stream sediments, distributed along an area of about 10 km^2 not directly influenced by external pollution, were collected and analysed for total concentration of Hg, As and Sb. The highest contents of Hg, As, and Sb were found in those soils developed in volcanic rocks: up to 211, 63.3 and 12 mg/kg, and 286, 276.19, and 109 mg/kg respectively, whereas the lowest values were found in soils formed above the sedimentary rocks (0.28, <1, 1 and 0.07,1, <1 mg/kg, respectively). The stream sediments had Hg and As concentrations up to 64.6 and 42.6 mg/kg respectively whereas Sb was always <1 mg/kg. The areal distribution of the three elements was visualised by dot-maps. Mercury showed a heterogeneous distribution in all three geological matrices, whereas As was more enriched in volcanic soils. Antimony revealed the highest concentrations in the calcareous-clay formations. According to these preliminary results, the mercury heterogeneous distribution, particularly in the top-soils and stream sediments, is probably related to the former mining activity, while As concentrations, as expected, depend on the lithological features.

Major, minor and trace elements distribution in the groundwater of High Agri Valley (southern Apennines): environmental constraints

Serena Panebianco[1,2], Michele Paternoster[1,3], Dario Buttitta[1,3], Antonio Caracausi[3], Roberto Buccione[1], Filippo Zummo[1], Giovanni Mongelli[1,2]

[1]*Università degli Studi della Basilicata, Dipartimento di Scienze, Potenza, Italia*
[2]*Istituto di Metodologie per l'Analisi Ambientale (IMAA), Consiglio Nazionale delle Ricerche (CNR), Potenza, Italia*
[3]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italia*

Keywords: Groundwater geochemistry; Water quality; High Agri Valley (southern Italy)

Groundwater quality depends on both natural processes (e.g., water-rock interaction) and anthropogenic activities (e.g., industrial and agricultural activities). The management of groundwater resources requires the assessment of hydro-geochemical characters in order to: (a) define water origin and migration patterns; (b) discriminate between geogenic and/or anthropogenic input (c) establish a geochemical baseline for the long-term environmental monitoring, crucial in these areas. Purpose of this work is the groundwater quality assessment of the High Agri Valley (HAV), one of the largest intermontane basin of southern Apennines characterized both by intense anthropogenic activities (i.e., hydrocarbon extraction by largest onshore oil field in Europe) and karstified and porous multilayer aquifers, respectively located on carbonate rocks and sediments of the Lagonegro Units. A total of 40 water samples were collected from springs and wells located at the main hydro-structures bordering the valley in order to determine chemical (major, minor and trace elements) and isotopic composition (dD and $d^{18}O$). All investigated water samples have a meteoric origin, although some springs show long and deep flow than the other ones, and a bicarbonate alkaline-earth composition, thus suggesting the carbonate hydrolysis as the main water-rock interaction process. Minor silicate dissolution processes were recognized in some water samples. Groundwater quality and its suitability for drinking use were evaluated counting data of this work and those by Paternoster et al. [2021], by comparing trace elements with their maximum admissible concentrations (MAC) of the Italian and European legislation guidelines. Our results demonstrated that HAV groundwater is chemically suitable for drinking use, showing no criticalities for potentially toxic metals. However, some isolated nitrate high levels, probably related to agricultural activity (i.e. organic fertilizer) have been recorded.

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Metal stable isotopes as tracers in environmental geochemistry: Ni isotope fractionation in mine-impacted environments

Roberta Parigi, Carol J. Ptacek and David W. Blowes

University of Waterloo, Department of Earth and Environmental Sciences, Waterloo, Ontario, Canada

Keywords: Metal stable isotopes; Ni isotopes; Sudbury (Canada)

As changes in metal stable isotope ratios are often associated with processes involved in the release, mobility, and fate of metals in natural systems, metal stable isotope analysis has been successfully applied to investigation of biogeochemical cycling of metals and metalloids in the environment [Romanek et al., 2010; Bullen, 2014; Wiederhold, 2015]. Although Ni stable isotope analysis has acquired recent attention, Ni stable isotope systematics is still at an early stage of development, and research focusing on Ni isotope fractionation associated with Ni attenuation processes is lacking.

The present research involved firstly, laboratory-scale studies examining the magnitude of the isotope fractionation associated with important Ni attenuation processes, including precipitation and adsorption, and subsequently, the application of Ni stable isotope analysis to investigate the processes influencing Ni release and attenuation at a mine site affected by extensive sulfide mineral oxidation. Ni isotope fractionation was measured during the precipitation of Ni-bearing secondary minerals under ambient conditions and in abiotic systems, and during synthetic Ni-contaminated groundwater interactions with sulfate reducing bacteria, which are commonly implemented in passive treatment remediation techniques. The Ni stable isotope signature associated with Ni removal by calcite under saturated flow conditions, characteristic of field settings, was also investigated. Finally, Ni stable isotope analysis was performed on pore-water extracted from a sulfide-oxidated tailings impoundment in Sudbury, ON, Canada for exploring the potential use of Ni stable isotopes as environmental tracers. The results of this early research suggest that the stable isotopes of Ni can be used to help determine the dominant metal attenuation processes which control Ni mobility in mine-impacted environments.

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Effects of hypoxia on biogeochemical cycling of nutrients and trace elements in a stratified estuarine system (Gulf of Trieste, northern Adriatic Sea)

Elena Pavoni[1], Elisa Petranich[1], Federico Floreani[1], Matteo Crosera[2], Gianpiero Adami[2], Jadran Faganeli[3], Stefano Covelli[1]

[1]*Università degli Studi di Trieste, Dipartimento di Matematica e Geoscienze, Italia*

[2]*Università degli Studi di Trieste, Dipartimento di Scienze Chimiche e Farmaceutiche, Italia*

[3]*National Institute of Biology, Marine Biology Station, Piran, Slovenia*

Keywords: Potentially toxic trace elements; Estauries; Timavo River (northern Italy)

Estuaries can be thought as a sedimentary trap leading to the accumulation of potentially toxic trace elements (PTEs) in sediments. However, biogeochemical processes at the sediment-water interface (SWI) may also be responsible for the release of dissolved PTEs and nutrients in the overlying water column affecting the water quality [Petranich et al., 2018; Garcia-Ordiales et al., 2020]. The estuarine system of the Timavo River (Gulf of Trieste, northern Adriatic Sea) is a semi-closed aquatic environment where a long-lasting oxic-hypoxic interface along the water column occurred due to the scarce water circulation in the innermost sector [Pavoni et al., 2021]. To prevent bloom-forming and potential production of toxins and off-flavours, artificial mixing has been provided with a bubble plume installation connected to pressurised air and built on the sediment surface aiming at re-oxygenating the water column. The aim of this research was to evaluate the behaviour of PTEs (As, Cr, Hg, Fe, Mn, Ni, Pb, V) and nutrients (NO_3, NO_2, NH_4 and SRP) along the water column and at the SWI before (June) and during (September) the activation of the forced aeration system. Water samples were collected at different depths along the water column, *in situ* benthic chamber experiments were performed at the SWI and short sediment cores were sampled to investigate both the sediment and porewater. Dissolved oxygen decreased along the water column, especially in June when hypoxia (2.29 mg/L) and reductive conditions (-58 mV) were observed at the bottom resulting in increasing dissolved PTE and nutrient concentrations. Accordingly, a gradual oxygen depletion was observed in the benthic chamber testifying to intense organic matter remineralisation processes. Moreover, the highest concentrations of dissolved PTEs in porewater were restricted to the top of the sedimentary sequence, especially in June when hypoxic conditions may promote PTE and nutrient effluxes from the sediment to the water column.

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Geochemical investigation of trace metal pollutants in the Oreto river, Palermo (Italy)

Brigida Pedone[1], Walter D'Alessandro[2], Filippo Brugnone[1], Lorenza Li Vigni[1], Francesco Parello[1], Sergio Bellomo[2], Lorenzo Brusca[2], Fausto Grassa[2], Vincenzo Prano[2], Sergio Calabrese[1,2]

[1]Università degli Studi di Palermo, Dipartimento di Scienze della Terra e del Mare, Italia
[2]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italia

Keywords: Trace metal pollutants; River geochemistry; Kemonia, Papireto and Oreto rivers (southern Italy)

In the past, three main rivers, named Kemonia, Papireto and Oreto, were present in the plain of Palermo, in north-western Sicily. Today, only the latter one has been preserved from the unregulated urban expansion. Fortunately, over the last ten years, attention and consciousness towards the Oreto river and its delicate ecosystem has grown considerably, also thanks to many associations and citizens' committees involved in protecting, preserving and valorising the precious area. In this context, our study is focused on a hydrogeochemical investigation of its surface water quality. The Oreto river flows for about 20 km within a catchment area of about 130 km^2. Over the past three years, numerous water sampling campaigns have been carried out in order to measure the main physical-chemical parameters (EC, T, DO, Eh and pH) and analyse the major constituents (Na, K, Ca, Mg, S, Cl, F, N, Alkalinity) together with a large suite of trace elements (including those potentially toxic). Sampling sites include the river mouth, several springs, poorly purified (or untreated) urban sewage discharges, and the main river confluences. Waters are of bicarbonate-alkaline earth composition, as a result of water-rock interaction processes and reflect the dominance of limestone sequences outcropping in the area. The effects of anthropogenic pressure on the river system become more evident in urban areas, where untreated sewage flows have a significant impact on water quality: negative Eh values, decrease in dissolved oxygen, increase in EC and nitrogen species. Many of the trace elements (Cu, Pb, Ni, Cr, Fe, Al, Sb and Sn) also show increasing trends from the springs to the estuary, highlighting the fingerprint of the anthropogenic sources.

Mercury speciation in contaminated coastal sediments using thermo-desorption technique: matrix effects

Elisa Petranich[1], Sergio Predonzani[2], Alessandro Acquavita[2], Nikolay Mashyanov[3], Stefano Covelli[1]

[1]*Università degli Studi di Trieste, Dipartimento di Matematica e Geoscienze, Italia*

[2]*Agenzia Regionale per la Protezione Ambientale del Friuli Venezia Giulia (ARPA FVG), Udine, Italia*

[3]*Lumex-marketing, St. Petersburg, Russia*

Keywords: Mercury speciation; Coastal sediments; Trieste Gulf (northern Italy)

The determination of total mercury (Hg) content in a solid matrix (i.e., soils and sediments) does not provide any information on its potential toxicity [Biester et al, 2002], especially when the risk assessment in contaminated areas is required. It is well known that the toxicological effect of Hg is highly dependent on its speciation, thus the identification of the chemical species is the key to interpret its biogeochemical behaviour [Bollen et al., 2008]. An easy-to-use technique for the rapid identification and quantification of Hg species in the solid matrix is based on thermal desorption (pyrolysis) of Hg compounds at different temperatures coupled to a continuous determination by atomic absorption spectrometry (AAS). The single Hg species that desorb at a specific temperature may be easily recognized [Biester and Scholz, 1997]. In this work, the pyrolysis spectra of numerous natural and commercial pure compounds, mixed with synthetic and natural matrices, were investigated. The final aim was to apply the analytical approach to Hg contaminated sediments characterized by the presence of unknown Hg species. The pyrolysis coupled to AAS was performed into a double chamber (PYRO-915+ coupled to Lumex RA-915M Mercury Analyzer) [Mashyanov et al., 2017] with air as gas carrier to flush Hg vapours through the analytical line. Selected sediment samples from the Gulf of Trieste (northern Adriatic Sea), contaminated by long-term Hg mining activities [Covelli et al., 2001], were then analyzed. The results revealed the presence of two peaks with distinct temperatures of desorption (~250 and 325 °C). The highest temperature corresponds to the mostly insoluble α-HgS (red cinnabar) compound whereas the lowest temperature is related to other Hg species (e.g., β-HgS and/or α-FeOOH≡Hg), which may include Hg associated with more mobile and potentially bio-accessible species if compared to α-HgS.

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Attenuation of Volatile Organic Compounds (VOCs) in a simulated landfill cover soil system

Antonio Randazzo[1,2], Stefania Venturi[1,2], Francesca Zorzi[1], Gabriele Bicocchi[1,2], Fabio Tatàno[3], Franco Tassi[1,2]

[1]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Italia*

[2]*Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia*

[3]*Università degli Studi di Urbino Carlo Bo, Dipartimento di Scienze Pure e Applicate, Italia*

Keywords: Volatile Organic Compounds; Simulated landfill; Carbon isotopes

Landfill gas (LFG) emissions, consisting mainly of CO_2 and CH_4, include low amounts of non-methane volatile organic compounds (VOCs), having a significant impact on air quality. Despite most of LFG is generally recovered by the implemented gas collection and extraction systems, a relevant amount remains uncollected and escapes to the atmosphere. Landfill cover soils act as full-scale bioreactors able to reduce diffuse CH_4 emissions, while their effective role in mitigating VOCs emissions is still debated. In this study, a simulated landfill experiment was conducted to investigate the degradation processes affecting VOCs. A hand-made LFG, generated by the anaerobic digestion process of food waste in a dedicated lab-scale digester, was forced to flow up through a typical section of a final landfill cover soil (H = 60 cm, d = 15 cm) consisting of silty sand. The experiment lasted for 23 days. Series of gas samples were periodically collected each 10 cm along the soil column and from the digester, and were consequently analyzed in terms of VOCs, main components, and $^{13}C/^{12}C$ ratios of CH_4 and CO_2. Overall, LFG-related components (CO_2, CH_4, and H_2) and VOC concentrations decreased over time and toward the upper part of the soil column due to the progressive exhaustion of anaerobic digestion process and air dilution, respectively. CH_4 was efficiently degraded at oxidizing conditions as also confirmed by the distribution of $\delta^{13}C\text{-}CH_4$ and $\delta\,^{13}C\text{-}CO_2$ values along the soil profile. Alkanes resulted more recalcitrant than aromatics, terpenes, and O-substituted compounds. Alkylated aromatic and branched alkane compounds were the most degraded among those of their respective organic groups. Cyclics, alkenes, and halogenated compounds were mainly found in the headspace of the digester. These preliminary data showed that this kind of lab-scale experiments could represent a reliable approach to deeply investigate the behavior of VOCs in landfill cover soils under controlled conditions.

Local natural background levels in groundwater for selected redox-sensitive species in Lombardy region (N Italy)

Marco Rotiroti, Chiara Zanotti, Mariachiara Caschetto, Tullia Bonomi, Letizia Fumagalli

Università degli Studi di Milano-Bicocca, Dipartimento di Scienze dell'Ambiente e della Terra, Italia

Keywords: Redox-sensitive species; Groundwater geochemistry; Lombardy (northern Italy)

Although natural background levels (NBLs) in groundwater are often assessed through a unique value per groundwater body, accounting for spatial hydrogeochemical heterogeneity can be more adequate, giving rise to the calculation of the so-called "local" NBLs. This work presents the assessment of local NBLs for the redox-sensitive species As, NH_4, Fe and Mn in the groundwater bodies of Lombardy region, N Italy. Local NBLs were calculated using a methodology that essentially involved a hybridization of preselection [Hinsby et al., 2008] and probability plot [Sinclair, 1974] approaches. A redox zonation, performed by a multivariate statistical analysis, led to the spatialization of local NBLs. Besides, a conceptual hydrogeological and hydrochemical model was developed and improved for driving the calculation and interpretation of local NBLs. The resulting NBLs interpreted along with the insights from the conceptual model allowed to pair to a specific local NBL, generating natural hydrogeochemical processes or conditions. Results showed that NBLs for arsenic were up to 291 µg/L, reached in groundwaters under methanogenesis, a condition related to the prolonged degradation of peat buried in aquifer sediments in the lower Po Plain. Ammonium NBLs up to 6.62 mg/L resulted by the upwelling of fluids from deep sediments, likely hosting petroleum systems, facilitated by tectonic structures; ammonium NBLs up to 4.48 mg/L were generated as the accumulation of by-products of peat degradation in the lower Po Plain. Iron and manganese NBLs up to, respectively, 6.0 and 1.51 mg/L were generated by the reduction of Mn and Fe oxides within river valleys, mostly the Po River valley. The evaluation of local NBLs, and their association to generating processes or conditions, achieve a step forward from the use of a single NBL per groundwater body, improving the existing decision-support tools for a sustainable and accurate groundwater management and protection.

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Indoor Radon Measurements in public schools and dwellings in the Ciampino municipality (Greater Rome Metropolitan Area) and its risk perception assessment

Alessandra Sciarra[1], Luca Pizzino[1], Gianfranco Galli[1], Livio Ruggiero[1],
Stefano Graziani[2], Tullio Ricci[1], Rosella Nave[3], Stan Eugene Beaubien[2],
Giancarlo Ciotoli[4,1], Sabina Bigi[2]

[1] *Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Sismologia e Tettonofisica, Roma, Italia*
[2] *Università Sapienza di Roma, Dipartimento di Scienze della Terra, Italia*
[3] *Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano, Italia*
[4] *Istituto di Geologia Ambientale e Geoingegneria (IGAG), Consiglio Nazionale delle Ricerche (CNR), Roma, Italia*

Keywords: Indoor radon measurements; LIFE-Respire project; Ciampino (central Italy)

Radon (^{222}Rn) is a natural radioactive gas produced by the decay of its parent nuclide (Uranium) in bearing rocks and soils. Inhalation of radon gas poses a serious risk for human health and the World Health Organization (WHO) stated the doubtless correlation between long exposure to radon gas and lung cancer [https://www.who.int/news-room/fact-sheets/detail/radon-and-health]. In the framework of the LIFE-Respire project, 76 indoor radon measurements in private and public buildings were performed in the Ciampino municipality. Indoor radon concentration (IRC) was measured by using passive nuclear track detectors (CR-39) and analysed using RADOSYS system at INGV Radionuclides laboratory. Measurements were carried out in winter and summer seasons to assess the range of seasonal fluctuations, as recognised elsewhere [e.g. De Francesco et al., 2010]. IRC shows substantial increase of maximum indoor values in winter (up to 1575 Bq/m^3) that are two times higher than those measured in the summer period (up to 764 Bq/m^3). The annual mean and median values (283 and 203 Bq/m^3, respectively) are both below the EU recommended limit of 300 Bq/m^3. A questionnaire on radon risk perception was designed for the specific context of the LIFE-Respire project and distributed in a sample of residents and students in the Municipality of Ciampino to measure, among many other aspects, the salience of the hazard, knowledge of the hazard and of hazard mitigation strategies, perceived preparedness of and trust in officials, sources of received information and preferred methods of receiving information, and the level of interest in the project approach (including remediation measures).

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Sediment quality of the Ridracoli fresh water reservoir: insights from aqua regia digestion and sequential extractions

Simone Toller[1], Valerio Funari[2], Denis Zannoni[3], Ivo Vasumini[4], Enrico Dinelli[5]

[1]*Università di Parma, Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale, Italia*
[2]*Consiglio Nazionale delle Ricerche, Istituto Scienze Marine, Dipartimento di Scienze della Terra e Tecnologie per l'Ambiente, Bologna, Italia*
[3]*Università di Bologna, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Ravenna, Italia*
[4]*Romagna Acque Società delle Fonti S.p.a., Forlì, Italia*
[5]*Università di Bologna, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Italia*

Keywords: Potentially harmful elements; Sediments; Ridracoli catchment (central Italy)

The impact of heavy metal pollution and elements accumulation on reservoirs is a matter of concern worldwide. In previous studies, we assessed the chemical compositions and seasonal changes in the water body [Toller et al., 2020] and characterized the sediments from Ridracoli catchment and surrounding areas [Toller et al, 2021]. The Ridracoli reservoir, an artificial basin for freshwater storage on the northern Apennines in Italy, is studied to highlight its importance as a drinkable water resource and for monitoring and maintaining its quality. In general, sediment composition was found to be consistent with a mixture of carbonate and clay, in agreement with the background composition. Aqua regia digestion data (AR) was studied along with the sequential extraction procedure data (SEP) [Sahuquillo et al., 1999; Rauret et al., 2000] on selected samples to evaluate the mobility of elements, in particular potentially harmful elements (PHEs). Therefore, this work highlights the importance of combining total and pseudo-total concentrations with SEP data in order to understand the partition and stability of elements in the different phases to which they are linked [Frémion, 2017; Wang, 2021]. The aims of this work are: I) to study relationships among elements by applying statistical methods; II) to compare with local sediments, literature data and limits proposed by the Italian legislation; III) to evaluate the extractability degree concerning the total and pseudo-total contents and understand stability and element mobility between solid and liquid phases inside the reservoir; and IV) to highlight the behaviour of potentially harmful elements (PHEs) in different exchangeable, reducible, oxidizable and residual fractions from sequential extractions.

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Combining forced ventilation with suitable inner coatings to reduce indoor radon levels in a scale model room

Paola Tuccimei[1], Gianfranco Galli[2], Michele Soligo[1], Martina Mattia[1], Manuela Portaro[1], Alessandra Briganti[3]

[1]*Università degli Studi Roma Tre, Dipartimento di Scienze, Italia*

[2]*Istituto di Geofisica e Vulcanologia, Sezione di Sismologia e Tettonofisica, Roma, Italia*

[3]*Istituto di Geologia Ambientale e Geoingegneria (IGAG), Consiglio Nazionale delle Ricerche (CNR), Roma, Italia*

Keywords: Indoor radon measurements; Tufo di Gallese; Inner and outer coatings

In the frame of "Radon rEal time monitoring System and Proactive Indoor Remediation" (RESPIRE), a LIFE 2016 project funded by the European Commission, the contribution of building materials of volcanic origin to indoor radon concentration was investigated. A very porous ignimbrite "Tufo di Gallese from Vico volcano (central Italy), was used to construct a scale model room of 62 cm × 50 cm × 35 cm (inner length × width × height, respectively) to study the effects of inner and outer coatings on radon levels [Lucchetti et al., 2020]. The combined influence of forced ventilation at different flow rates was investigated, too. Experiments showed that outer covers (plastic films) promote the accumulation of indoor radon, reducing the air exchange through the chamber walls, while inner covers (panels of painted plasterboard) are very effective to cut ^{220}Rn (thoron) levels, but less efficient for ^{222}Rn (radon). Outdoor air introduction in the model room enhanced the barrier effect of inner covers, showing a direct correlation between air flow velocity and radon decrease. On the other hand, indoor air extraction was less successful than air introduction in reducing radon activity concentrations. Final experiments were carried out without any coatings to evaluate the effect of ventilation (air introduction and extraction) alone. These tests were modelled with a modified version of Fick's second law to describe the diffusion of radon gas through the chamber walls. These results suggest that the combined use of suitable coatings on the inner walls of a building and outdoor air introduction at adequate rates are a good strategy for addressing radon mitigation actions.

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Diffusive CH_4 emissions from wetlands: the Porta and Massaciuccoli (northern Tuscany, central Italy) case studies

Stefania Venturi[1,2], Franco Tassi[1,2], Jacopo Cabassi[2], Antonio Randazzo[1,2], Marta Lazzaroni[1,2], Francesco Capecchiacci[1,2,3], Barbara Vietina[4], Orlando Vaselli[1,2]

[1]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Italia*

[2]*Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia*

[3]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano, Napoli, Italia*

[4]*Comune di Montignoso, Ufficio Ambiente, Massa Carrara, Italia*

Keywords: Wetlands; Diffusive methane emissions; Porta and Massaciuccoli (central Italy)

Wetlands are among the main natural sources of CH_4 emissions to the atmosphere. Nevertheless, large uncertainties still affect the estimates of their overall contribution at both local and global scales due to several knowledge gaps on how environmental drivers shape CH_4 emissions from these delicate ecosystems. In this work, we present CH_4 diffusive fluxes, along with chemical and isotopic data on dissolved ionic and gaseous species, from two wetlands located in northern Tuscany (Italy), i.e. (i) Porta, a small wetland invaded by *Phragmites australis* reeds and affected by reed die-back syndrome (RDBS) since 2016, and (ii) Massaciuccoli, a wide marsh area including both open water basins and channels affected by seawater intrusion and eutrophication. Both wetlands were found to be net sources of CH_4 to the atmosphere. The magnitude of CH_4 emission at the water-air interface was governed by CH_4 production and consumption rates, which were depending on (i) water temperature and availability of labile carbon substrates, and (ii) water column depth, wind exposure, and dissolved O_2 contents, respectively. Our results suggested that reed beds enhance diffusive CH_4 fluxes, likely as a consequence of wind sheltering and availability of plant litter. The latter provides labile organic matter promoting acetoclastic methanogenesis as suggested by carbon isotopic signatures of CH_4. These findings indicate that a relevant portion of CH_4 emissions from waterbodies is likely underestimated in global carbon budgets, with relevant implications for Earth system and climate models. Moreover, while wetlands are among the most threatened ecosystems on Earth, the relationship between RDBS and high CH_4 diffusive fluxes underlines the urgent need of wetland protection and restoration interventions.

Determination of gaseous elemental mercury (GEM) emissions by a non-stationary static accumulation chamber.
The case study of Portoscuso (South-West Sardinia)

Giorgio Virgili[1], Maurizio Guerra[2], Antonella Vecchio[2], Federico Floreani[3,4], Elisa Mariani[5], Gianfranco Mulas[6], Stefano Covelli[3], Orlando Vaselli[7], Luca Spinelli[1]

[1]*Thearen srl, Torino, Italia*

[2]*Istituto Superiore per la Protezione e la Ricerca Ambientale ISPRA, Dipartimento per il Servizio Geologico, Roma, Italia*

[3]*Università degli Studi di Trieste, Dipartimento di Matematica e Geoscienze, Italia*

[4]*Università degli Studi di Trieste, Dipartimento di Scienze della Vita, Italia*

[5]*Libera professionista, Roma, Italia*

[6]*Comune di Portoscuso, sud Sardegna, Italia*

[7]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Italia*

Keywords: Gaseous Elemental Mercury; Non-stationary static accumulation chamber; Portoscuso (Sardinia)

This work describes the methodology based on a non-stationary static accumulation chamber used for measuring the GEM emissions at the soil-atmosphere interface in some residential and agricultural areas of the Portoscuso Municipality (South-West Sardinia). After a preliminary risk assessment of soil contamination, the investigated areas highlighted potential significant human health risks for volatilization pathways related to total Hg content in the soil. The aim of this study is to use the GEM emission rate to estimate indoor and outdoor human exposure according to the specific use of the areas. Acceptable GEM emissions (AGEM), i.e. maximum emissions associated with an acceptable human exposure and health risk, were defined accordingly and compared with measured ones.

The measured GEM emissions probably constitute the sum of two contributions:

- a real flux of GEM *"through the* soil-atmosphere *interface"*. This flux is originated by the presence of sources (both natural and/or related to potential contamination) in the first meters of depth and is regulated by mainly advective mechanisms;
- a component produced *"at the* soil-atmosphere *interface"*, as a response to the action of UV radiation on divalent Hg (II) in soil particles.

In this study the contribution of each of these two components has not been evaluated; however the main results showed, at the scale of the single sample representative area (Thiessen polygon), few values (8 out of 163, about 5%) exceeding the AGEM values for the indoor scenario. These results are poorly indicative of a real unacceptable risk, given their extremely punctual extent not representative of a long-term human exposure. Conversely, GEM emissions for each macro-area showed a general compliance with acceptable thresholds emission (AGEM) computed for both outdoor and indoor scenarios.

Further investigations will be aimed at discriminating the two components that originate the measured GEM flux values.

Geochemical study of surficial waters from the wetland north of Florence

Gregorio Viti[1], Franco Tassi[1,2], Orlando Vaselli[1,2]

[1]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Italia*

[2]*Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia*

Keywords: Wetlands; Water geochemistry; Florence (central Italy)

Wetlands have always played a fundamental role in life, hosting the greatest biodiversity on Earth. These areas also represent an important source of water and food, as well as an aid against global warming thanks to the storage of carbon. Wetlands are ecosystems sensitive to anthropogenic pressure and, for this reason, they are gradually disappearing in recent years due to human expansion over nature. Based on geochemical analysis, a survey on the health of the wetlands sited north of the city of Florence (Italy) was carried out. The main purpose of this study was to define how much anthropogenic pressure affects these wetlands located in the rural-urban fringe. The data obtained from the analysis of nitrogenous species showed how the anthropogenic pressure makes its presence felt mainly inside the ditches, since during their course they obtain water from urban discharges. On the other side, the latter exerted less pressure on the lakes, where the relatively high contents of nitrogenous species derive mainly from the use of nitrate-based fertilizers used in agriculture. The analyses on the major dissolved species and on heavy metals showed anomalies in Na^+, Cl^-, SO_4^{2-}, Fe and Mn species in some sites, highlighting the impact of the textile industries of Prato and agricultural activities on wetlands chemistry. Volatile organic compounds were also analyzed to provide a first report on the concentrations of these species in the study area. To evaluate the temporal evolution of the wetland's chemical status, data from the present study were compared with those from previous surveys. A clear improvement in the situation was observed in most of the investigated sites, thanks to reclamations and improvements in the exploitation of agricultural land that have taken place over time. The areas near the textile industries of Prato are an exception, showing how this activity can largely impact the ecosystems in the neighbouring area.

HEAVEN: a stairway for risk assessment from radioactive volcanic emissions

Nunzia Voltattorni[1], Salvatore Giammanco[2], Gianfranco Galli[1], Andrea Gasparini[1], Giovannella Pecoraino[3]

[1]*Istituto Nazionale di geofisica e Vulcanologia, Sezione di Sismologia e Tettonofisica, Roma, Italia*
[2]*Istituto Nazionale di geofisica e Vulcanologia, Sezione di Catania - Osservatorio Etneo, Catania, Italia*
[3]*Istituto Nazionale di geofisica e Vulcanologia, Sezione di Palermo, Italia*

Keywords: HEAVEN project; Potentially harmful trace/radioactive elements; Mt. Etna (southern Italy)

Volcanoes release magma-molten rock, gases and water within the earth that may interact with human biological systems. Because of the range of materials that are emitted during eruptions, the consequent effects on human health are diverse. Contact may occur dramatically and immediately for people living close to a vent, but effects on health may occur slowly and/or at great distances from the volcano as a result of dispersal of volcanic material [Weinstein et al., 2013]. Mt. Etna is the largest stratovolcano in Europe and one of the most active in the world, emitting many hazardous soil gases through diffuse flank emissions. Among those, carbon dioxide (CO_2) and radon (^{222}Rn) are the most abundant and harmful. In recent years, many in-soil radon measurements on Mt. Etna showed a typical background level concentration of <1000 Bq/m^3 [Neri et al., 2016]. Anomalous soil degassing (up to 60,000 Bq/m^3) is particularly strong in the east and southwest flanks of the volcano [Burton et al., 2004], characterized by continuous tectonic deformations and gravitational collapses. The SE flank of Etna Volcano is also characterized by a higher incidence of Amyotrophic Lateral Sclerosis (ASL) and Multiple Sclerosis (MS) in local people as reported by several medical studies [Nicoletti et al. 2020; Boumediene et al. 2019]. The primary goal of the HEAVEN project - Hazard from EtnA Volcanic EmissioNs (funded by INGV Dynamic Planet project 2021) is to define health hazards related to volcanic emissions of potentially harmful trace/radioactive elements. In the case of radiogenic elements, dispersion models of radon gas emission from soils through faults onto the ground surface and into houses is important particularly inside the clusters of incidences of ALS and MS. First preliminary results are encouraging to deepen the relationship between health risk and volcano emissions.

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Assessing the natural background levels of potentially toxic elements in groundwater from a former asbestos mine in Serpentinite (Balangero, north Italy): the influence of nitrates

Giacomo Zatti[1], Massimo Bergamini[2], Elisa Sacchi[1]

[1]*Università di Pavia, Dipartimento di Scienze della Terra e dell'Ambiente, Italia*
[2]*R.S.A. Srl, Balangero, Torino, Italia*

Keywords: Potentially toxic elements; Asbestos; Balangero mine (northern Italy)

The identification of natural background levels (NBLs) for potentially toxic elements (PTEs) in groundwater from mining areas is a challenging task. In these environments, the naturally high background concentrations may be further increased by anthropogenic activities. Nitrates are listed as indicators of anthropogenic influence by the Italian guidelines for NBL evaluation [ISPRA, 2018], and a pre-selection NO_3^- concentration of 37.5 mg/L is indicated, higher than other regulations. The Balangero mine, a "Contaminated Site of National Interest", is located ~30 km NW of Turin. The mine, hosted in the serpentinised outer rim of the Lanzo Massif, operated from the 1920s to the 1990s for the extraction of chrysotile, becoming the largest asbestos mine in Western Europe. The dominant groundwater facies is Mg-HCO_3, tending to the Mg-SO_4 facies with increasing mineralisation. PTE concentrations are high, often exceeding the groundwater quality thresholds for Cr(VI), Ni, Mn and Fe. A preliminary assessment of PTEs NBLs was performed following the Italian guidelines with some modifications. Based on all the available data, the NBLs were: Cr=39.3, CrVI=38.1, Ni=84, Mn=71.4, Fe=58.4, Zn=232 µg/L [Sacchi et al., 2019]. Using data from the last sampling, we investigated the influence of nitrates on the NBL values. Only Ni shows a significant correlation with nitrates, and its NBL depends on the NO_3^- value used as pre-selection criteria, changing from 57.6 to 58.6 to 35.2 µg/L for NO_3^- thresholds set to 37.5, 25 and 10 mg/L, respectively. Compared to literature data from similar environments [e.g. Apollaro et al., 2019], the higher Ni NBLs determined at Balangero correspond to the NBL determined on the latter dataset (56.7 µg/L), supporting the conclusion that nitrates fuel up the natural water-rock interaction process. Results highlight the need for a partial rethink of the guidelines for the assessment of NBLs in naturally enriched environments.

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SESSION 3 - ISOTOPE GEOCHEMISTRY

Conveners:
Enrico Cannaò (Università degli Studi di Milano), Barbara Nisi (CNR-IGG),
Luigi Dallai (Università di Roma La Sapienza)

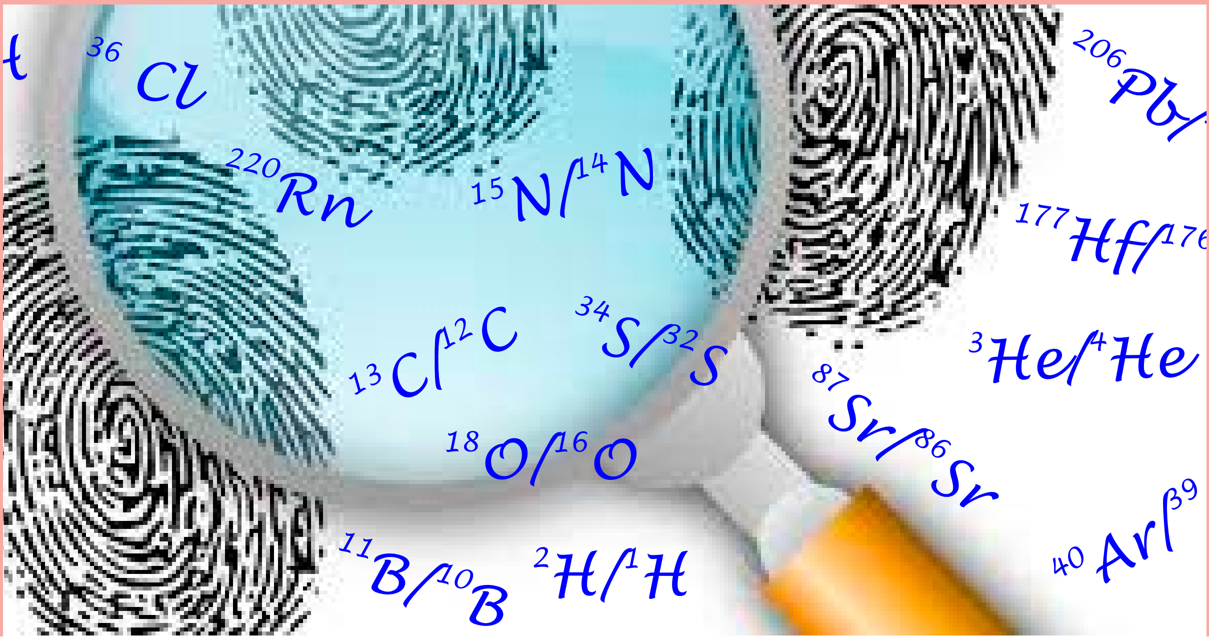

Figure caption: Tracing environmental matrices. Graphics design by Barbara Nisi

Carbon dioxide Earth degassing, heat flux and earthquakes: the case of the Apennines

Giovanni Chiodini

Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Italia

Keywords: CO_2 Earth degassing; Carbon isotopes; CO_2 emissions vs. earthquakes

The active tectonic zones of the Earth are often characterized by a diffuse process of CO_2 emission (tectonic CO_2). Estimating the tectonic CO_2 emission is crucial for determining the global CO_2 emission from inorganic, geological sources. Preliminary estimates suggest that the global tectonic CO_2 emission could be comparable, if not greater, to the emissions from active volcanoes. The balance of the carbon species dissolved in the waters of large aquifers is an excellent tool for measuring this diffuse emission because it potentially allows the measurement of the average flux affecting large areas, coinciding with the extension of the aquifers (tens to hundreds of km^2 in Apennines). The method consists in (i) determining the different sources of the dissolved carbon through carbon isotopes, (ii) computing the concentration of the deeply derived CO_2, (iii) estimating the average flux throughout the aquifer basins coupling geochemical and hydrogeological data. The method applied to peninsular Italy indicates that the specific fluxes of CO_2 are greater than the baseline of the geothermal zones of the world and that the emission of tectonic CO_2 is higher than the total CO_2 emitted by the Italian volcanoes (Etna, Stromboli, Campi Flegrei, Vesuvius, Vulcano, etc.). In the Apennines there is a close relationship between CO_2 dissolved in groundwater and the heat flux suggesting that (i) geothermal heat is supplied to the aquifers by the upwelling of 'hot' fluids, the same ones that cause the regional CO_2 anomaly and that (ii) the 'advective' heat flux is the dominant form in the region (with values up to 200-300 mW m^{-2}). Finally, some examples suggest a close areal and temporal relationship between the CO_2 emission and the earthquakes in the Apennines.

New computational evidence of source below Monte Vulture volcano (preliminary results)

Dario Buttitta[1,2], Antonio Caracausi[2], Michele Paternoster[1,2]

[1]*Università degli Studi della Basilicata, Dipartimento di Scienze, Potenza, Italia*
[2]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italia.*

Keywords: Noble gas isotopes; Monte Carlo simulation; Mt. Vulture (southern Italy)

Mount Vulture is a Pleistocene volcanic complex in the southern part of the Apennine chain (Italy). Notwithstanding the last volcanic eruption occurred about 140 ky ago, large amounts of magmatic gases are still emitted from the volcanic edifice. Its products have peculiar petrologic characteristics, not least the trace element pattern and isotopic features of rocks, minerals and the hosted fluid inclusions that are intermediate between intraplate and subduction-related signatures. Here, we will discuss new Helium (He)-Argon (Ar) isotope data, in fluid inclusions from clinopyroxene and olivine phenocrysts from Mt. Vulture. The main topics are to figure out 1) the He isotopic signature of the mantle feeding the Mt. Vulture activities and/or 2) the secondary processes that could modify the He pristine signature before magma eruptions. We show a reverse modelling, based on disequilibrium open-system degassing with diffusive fractionation process to reconstruct the pristine geochemical signature (noble gas and carbon concentrations) of the magmatic sources at Mt Vulture. Combining the degassing process with the mass-dependent fractionation we computed the evolution of the $^{3}He/^{4}He$, $^{4}He/^{40}Ar^{*}$ and $CO_2/^{3}He$ in a confined volume at depth. Using a Monte Carlo simulation and bound constrained optimization function we modelled the conditions that fit the values of the measured geochemical parameters in minerals from Mt Vulture (e.g.,$^{3}He/^{4}He$,$^{4}He/^{40}Ar^{*}$). Our early results show that the studied fluid inclusions are representative of two clusters corresponding to the storage of magmas at different pressures. The former reflects a shallower, that fits the depth of magma storage proposed by Beccaluva et al. [2002]. The latter, which corresponds to the fluid inclusions in xenoliths, is consistent with CO_2-rich magmas at higher pressures.

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Stable isotopes analyses of fossil- and bio-based plastics of eyewear sector: a preliminary characterization

Marco Calvi[1], Luca Adami[2], Luana Bontempo[3], Luca Fiori[2]

[1]*Certottica S.c.r.l. - Istituto Italiano per la Certificazione dei prodotti ottici, Longarone, Belluno, Italia*
[2]*Università di Trento, Dipartimento di Ingegneria Civile, Ambientale e Meccanica, Trento, Italia*
[3]*Unità di Tracciabilità, Centro di Ricerca e Innovazione, Fondazione Edmund Mach (FEM), San Michele all'Adige, Trento, Italia*

Keywords: Stable isotopes; Plastics and bioplastics; Eyewear companies

A preliminary study for the isotopic characterisation of plastics and bioplastics used in the eyewear sector is presented here. The isotopic ratios of C, H, N, O and S of different plastic parts of glasses, were determined. This approach could be effective to distinguish fossil-based plastic polymers from bio-based plastic polymers [Dos Santos et al., 2021; Berto et al., 2017; Suzuki et al., 2010] and put the basis for a first database of the eyewear sector. 25 samples were collected from different eyewear companies in 2021. Plastic sheets, frames and lenses were reduced into small pieces before analysis. So far, no studies have been conducted on fossil- and bio-based plastic materials used for glasses and on all the stable isotopes of the five bio-elements. First data underline the difference between $\delta^{13}C$ values of plastic derived from C3 and C4 plants as reported in Berto et al. [2017]. $\delta^{2}H$ shows a wide range of values (-198.2 ÷ -77.7‰) and could be also useful to distinguish petrol and bio-based plastics [Rogers et al., 2021]. $\delta^{15}N$ and $\delta^{34}S$ are worthy of note, because they are present in few samples.

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From isotopes to ice sheet dynamics: how new isotopic records from the TALDICE ice core reveal past events of East Antarctic ice sheet retreat

Ilaria Crotti[1,2], Barbara Stenni[1], Amaelle Landais[2], Aurélien Quiquet[2,3], Massimo Frezzotti[4], David Wilson[5], Mirko Severi[6], Florian Ritterbusch[7], Carlo Barbante[1,8]

[1]*Università Ca' Foscari Venezia, Dipartimento di Scienze Ambientali, Informatica e Statistica, Venezia, Italia*

[2]*Université Paris-Saclay, Laboratoire des Sciences du Climat et de l'Environnement LSCE/IPSL, CEA-CNRS-UVSQ, Gif-sur-Yvette, France*

[3]*NumClim Solutions, Palaiseau, France*

[4]*Università di Roma Tre, Departimento di Scienze, Roma, Italia*

[5]*University College London and Birkbeck, Institute of Earth and Planetary Sciences, United Kingdom*

[6]*Università di Firenze, Departimento di Chimica Ugo Schiff, Firenze, Italia*

[7]*University of Science and Technology of China, Hefei, China*

[8]*Instituto di Scienze Polari (ISP), Consiglio Nazionale delle Ricerche (CNR), Venezia, Italia*

Keywords: Ice cores; Stable isotopes; Wilkes Subglacial Basin (East Antarctic)

The growth and decay of marine ice sheets act as important controls on regional and global climate and sea level. The Wilkes Subglacial Basin ice sheet appears to have undergone thinning and ice discharge events during recent decades, but its past dynamics are still under debate. The aim of our study is to investigate past ice margin retreat of the Wilkes Subglacial Basin ice sheet during late Pleistocene interglacials with the help of new high-resolution isotopic records from the TALDICE ice core. New isotopic analyses in both ice and gas matrices of δD_{ice}, $\delta^{18}O_{ice}$, $\delta^{15}N$, $\delta^{18}O_{atm}$, $\delta^{18}O/N_2$ and ^{81}Kr allow us to define the TALDICE deep1 chronology for the deeper part of the core (below 1438 m depth) and to extend the age scale back to MIS 10.1. The novel $\delta^{18}O_{ice}$ signal reveals that interglacial periods MIS 7.5 and 9.3 are characterized by a unique double-peak feature, previously observed for MIS 5.5 [Masson-Delmotte et al., 2011], that is not seen in other Antarctic ice cores. Combining glaciological evidence, an offshore Wilkes Subglacial Basin sediment core record and GRISLI ice sheet modelling experiments, we provide an interpretation of this peculiar record. Our results indicate that the interglacial double-peak $\delta^{18}O_{ice}$ signal could reflect Talos Dome site elevation decrease during the late stages of interglacials due to Wilkes Subglacial Basin retreat events. These changes coincided with warmer Southern Ocean temperatures and elevated global mean sea level, confirming the sensitivity of the Wilkes Subglacial Basin ice sheet to ocean warming and its potential role in sea-level change.

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In situ U-Pb and Hf isotopes analyses on zircon from the Giglio Island pluton

Alessandro De Leo, Federico Farina

Università degli Studi di Milano, Dipartimento di Scienze della Terra, Milano, Italia

Keywords: U-Pb and Hf isotopes; Zircon; Giglio Island pluton (central Italy)

The monzogranitic pluton of Giglio Island in the Tuscan Archipelago (Italy) is a relatively poorly studied intrusion belonging to the Tuscan Magmatic Province (TMP), an association of intrusive and effusive magmatic rocks formed between 14 and 0.3 Ma. New LA-ICP-MS geochronological U-Pb and Hf isotopic data were obtained from zircon grains separated from the two main texturally distinct units forming the intrusion: the outer, foliated Pietrabona facies (PBF), and the inner porphyritic Arenella facies (ARF). We defined from U-Pb dating an emplacement age for the Giglio intrusion of 5.448 ± 0.030 (2SE) Ma (weighted mean on 80 analyses, ^{206}Pb/^{238} U ages, Th disequilibrium corrected), improving the previously published age. Although individual spot ages are indistinguishable within error, the obtained weighted mean ages for the two facies are different, 5.493 ± 0.034 (49 analyses) for PBF, and 5.309 ± 0.060 (31 analyses) for ARF, thus suggesting that the pluton formed incrementally. We developed a robust method for the determination of Hf isotopic composition in zircon by LA-MC-ICP-MS obtaining crustal values of initial εHf comprised between -3.5 and -11.9 (2SE≈1). No differences between the two facies are apparent, however each sample exhibits a large Hf isotopic heterogeneity that is statistically significant compared to the repeatability obtained for reference zircons. Such variability suggests that different crustally-derived magmas contributed to the magmatic evolution of the pluton, advocating for a complex mechanism of melt production, ascent and final emplacement.

SESSION 3 - Isotope Geochemistry

Ten years of oxygen and hydrogen isotopic composition of daily precipitation at Concordia station, East Antarctica

Giuliano Dreossi[1,2], BarbaraStenni[2], Mauro Masiol[1,2], Vittoria Posocco[2],
Carlo Barbante[1,2]

[1] *CNR Consiglio Nazionale delle Ricerche, Istituto di Scienze Polari, Italia*

[2] *Ca' Foscari Università di Venezia, Dipartimento di Scienze Ambientali, Informatica e Statistica, Venezia, Italia*

Keywords: Stable isotopes; Dome C precipitation; Concordia station (East Antarctica)

Here we present a 10-year (2008-2017) record of the isotopic composition of precipitation at Dome C. The winter-over personnel at Concordia Station have been continuously collecting daily precipitation since 2008: this represents a unique record of the isotopic composition of precipitation from the Antarctic Plateau. Snow is collected on a raised platform (height: 1 m) in the clean area of the station and analyzed for d^{18}O, dD and deuterium excess. A significant positive correlation between d^{18}O (dD) of precipitation and 2-m air temperature is observed at different temporal scale; the lowest temperature and isotopic values are preferentially observed during winters affected by a strongly positive Southern Annular Mode index [Stenni et al., 2016]. We have compared the isotopic data of Concordia samples with meteorological data from the Dome C AWS of the Programma Nazionale di Ricerche in Antartide (PNRA), as well as with the isotope-enabled atmospheric general circulation models ECHAM5-wiso and ECHAM6-wiso, in order to improve the understanding of the mechanisms governing the isotopic composition of precipitation on the Antarctic plateau, which are yet to be fully understood, as well as the post-depositional effects altering the pristine isotopic signal of precipitation. The comprehension of these physical processes is fundamental for reconstructing past temperature variations using the isotopic records from ice cores drilled in low accumulation areas of Antarctica [Casado et al., 2018], e.g., the upcoming Beyond EPICA drilling at Little Dome C. Very few temporal relationships between temperature and snow isotopic composition, mostly limited in time or sampling frequency, have been calculated, while spatial relationships have been traditionally used to reconstruct past temperature from ice core isotopic records [Masson-Delmotte et al., 2008].

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Investigating the Hg isotopic footprint in groundwaters and cinnabar waste from the former mining area of Abbadia San Salvatore (Tuscany, central Italy)

Marta Lazzaroni[1], Orlando Vaselli[1,2,] Jacopo Cabassi[2], Barbara Nisi[2],
Daniele Rappuoli[3,4], Andrea Marchetti[5], Lisa Lancellotti[5]

[1]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia*
[2]*Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Firenze, Italia*
[3]*Unione dei Comuni Amiata Val d'Orcia, Unità di Bonifica, Piancastagnaio, Siena, Italia*
[4]*Parco Museo Minerario di Abbadia San Salvatore, Abbadia San Salvatore, Siena, Italia*
[5]*Università di Modena, Departimento di Chimica e Scienze Geologiche, Italia*

Keywords: Mercury; remediation action; Hg isotopes

Since 2010, at the abandoned Hg-former mining area of Abbadia San Salvatore, the efforts of local authorities have been addressed to increase the knowledge about the interaction between the environment and the ubiquitously distributed cinnabar waste. During the first part of 2021, before the beginning of remediation actions, 10 piezometer and spring waters were sampled and analyzed for major, minor solutes, As, Hg and Sb contents and Hg isotopes. Additionally, one calcine from Le Lame dump was investigated for Hg isotopes. The water samples were located inside and near the mining facilities and around the mining area. The main features for the selected waters can be summarized as follows: (i) relatively constant and high Hg concentrations during the monitoring period (from 2013 to 2021) and (ii) water circulation constrained in space and artificially-induced since the piezometers are located in a paleo-valley filled by calcine and other mining products. During sampling, the piezometers were purged and five aliquots were collected and filtered at 0.45 µm for: a) main dissolved species, b) As, Hg and Sb contents, c) water isotopes, d) sulfur-SO_4 isotopes, and e) Hg isotopes (in glass-ambered bottles with 0.75 mL of sub-boiled HNO_3). The replicates of the calcine were analyzed after mineralization, consisting in dissolving 0.2 g of sample in a mixed acid solution (v/v, 1 mL 65% HNO_3, 1 mL 6M HCl, 1 mL 37% HCl) in a microwave digester. The Hg isotopic ratios were measured via a Thermo Scientific Neptune MC-ICP-MS at the CIGS (Modena, Italy). Two standards were used inside the analysis sequence to correct the results: NIST SRM 3133 for Hg and NIST SRM 997 for Tl. The results show that δ^{199}Hg varies between -0.01 and +0.88‰, δ^{200}Hg between -0.03 and +1.44‰, δ^{201}Hg between -0.06 and +2.06‰, while δ^{202}Hg between -0.04 and +2.86‰. The lower isotopic values are always represented by the waste sample, while the water samples show a general enrichment in δ^{202}Hg isotope.

Evolution of $\delta^{11}B$ on tourmaline during prograde contact metamorphism in the thermal aureole of the Adamello batholith (Southern Alps, Italy)

Lorenzo Magnani, Federico Farina, Enrico Cannaò

Università degli Studi di Milano, Dipartimento di Scienze della Terra "Ardito Desio", Italia

Keywords: Boron isotopes; Tourmaline; Adamello batolith (northern Italy)

The Permian continental deposits of the Verrucano Lombardo formation (Southern Alps, Italy) are conglomeratic to pelitic redbeds deriving from the disgregation of vulcanites and of the Variscan basement. In the Forcel Rosso area, this formation underwent high-grade metamorphism and partial melting caused by the emplacement of the Adamello batholith during the Eocene. Tourmaline is ubiquitous in the pelitic and metapelitic layers up to migmatitic conditions and this allowed the investigation of the $\delta^{11}B$ evolution during the prograde metamorphic history. Tourmalines $\delta^{11}B$ values in the unmetamorphosed pelites show a wide difference between the extremely negative cores, and the positive rims. We interpret the cores to be detrital, while the rims were crystallized at low temperature in equilibrium with high $\delta^{11}B$ diagenetic or hydrothermal fluids. This $\delta^{11}B$ core-rim variation persists up to the greenschist facies while, from lower amphibolitic facies, tourmaline grains recrystallize and become more homogeneous with $\delta^{11}B$ values intermediate between cores and rims. Above the solidus, two types of metatexites were recognized based on the tourmaline $\delta^{11}B$ signatures. Type-I metatexites are characterized by euhedral tourmalines showing a very narrow range of positive $\delta^{11}B$ values. In Type-II metatexites euhedral tourmalines show slightly negative $\delta^{11}B$ composition. In the Forcel Rosso area, Type-I metatexites were formed in an isochemical closed system while Type-II metatexites required the influx of external fluids. Preliminar calculations suggest that the $\delta^{11}B$ signature of such external fluids was negative. Based on melt-fluid fractionation factors, if these fluids had been exsolved from a magmatic source, the coexisting melt would have had negative $\delta^{11}B$ signature outside the range of I-type granitoids. This advocates for a metamorphic source while excluding the influx of magmatic fluids from the nearby I-type Adamello pluton.

Is the deuterium excess in precipitation a reliable tracer of the moisture sources in the western Mediterranean? New insights from Tuscany (Central Italy)

Stefano Natali[1,2,3], Giovanni Zanchetta[2,4,5], Marco Doveri[3], Roberto Giannecchini[2,3,4], Ilaria Baneschi[3]

[1]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia*

[2]*Università di Pisa, Dipartimento di Scienze della Terra, Pisa, Italia*

[3]*Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Pisa, Italia*

[4]*Università di Pisa, Centro Interdipartimentale di Ricerca per lo Studio degli Effetti del Cambiamento Climatico, Pisa, Italia*

[5]*Istituto di Geologia Ambientale e Geoingegneria (IGAG), Consiglio Nazionale delle Ricerche (CNR), Roma, Italia*

Keywords: Rainwater isotopes; d-excess; Apuan Alps (central Italy)

The deuterium excess (*d*) is a function of $\delta^{18}O$ and $\delta^{2}H$ in water and it is used worldwide to constrain the moisture sources of precipitation, as it mainly depends on relative humidity and surface sea temperature at the evaporative sources. A case in point is precipitation deriving from vapor originating over the eastern Mediterranean Sea, characterized by the highest *d* (~22‰) compared to the global mean *d* in precipitation of 10‰. *d* values of ~15‰ found in precipitation across the western Mediterranean are interpreted as the result of mixing of Atlantic and Mediterranean vapor. Several studies proved the d-excess of precipitation may change depending on local processes [e.g. Wang et al., 2016]. In the western Mediterranean increasing *d* values were found in precipitation with altitude [Natali et al., 2021]. With the aim to investigate altitudinal variability of the d-excess in precipitation and to evaluate its reliability for tracing the moisture source in the western Mediterranean, we present the preliminary results of a study performed in the Apuan Alps (Tuscany, Central Italy). Monthly precipitation samples were collected from 2019 to 2021 in 5 sites at different altitudes. 19 single rain events were also collected. Higher *d* was found at higher altitudes. A monthly mean vertical d-excess gradient of +0.73‰/100m ($r^2 = 0.94$) was computed. These findings evidence the importance of local processes acting on the d-excess, thus limiting its reliability as a proxy of moisture sources.

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The contribution of clumped isotopes to paleoclimate and atmospheric research

Maura Pellegrini[1], Nina Albrecht[2]

[1]*Thermo Fisher Scientific, Milano, Italia,*
[2]*Thermo Fisher Scientific, Bremen, Germany*

Keywords: Clumped isotopes; Paleoclimate reconstruction; Carbonate and methane formation temperatures

Traditional stable gas isotope analysis (δD, $\delta^{13}C$, $\delta^{15}N$, and $\delta^{18}O$) are essential tools in many fields of Earth Sciences. They contribute to understanding atmospheric cycling, transport processes, source apportionment, and temperature reconstruction. Where these classical isotope approaches reach their limitations, clumped isotope geochemistry comes into play.

The term 'clumped isotopes' refers to isotopologues which have more than one substitution with a heavier isotope in their molecular structure, for instance $^{15}N^{15}N$ in nitrogen, $^{13}C^{18}O^{16}O$ in carbon dioxide, or $^{12}CH_2D_2$ in methane. One of the striking advantages of clumped isotopes is that their equilibrium distributions are solely dependent on formation temperature. It has been widely demonstrated that equilibrium clumping can be used to determine highly precise carbonate and methane formation temperatures [Eldridge et al., 2019; Fiebig et al., 2021]. Additionally, when combined with classical stable gas isotopes, clumped isotopes offer further dimensions to forensic source discrimination and the characterization of formation processes.

In this presentation, selected applications of isotope clumping in carbon dioxide, methane, oxygen, and hydrogen will be presented, highlighting their scientific usability in paleoclimate reconstruction and atmospheric research.

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Hydrological significance of $\delta^{18}O$ composition of speleothems and lakes carbonates from the central Mediterranean: a coherent hydrological framework from past interglacial periods

Eleonora Regattieri[1,5], Giovanni Zanchetta[2,4,] Russell N. Drysdale[3,], Biagio Giaccio[4], Ilaria Isola[5,1]

[1]*Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Pisa, Italia*
[2]*Università di Pisa, Dipartimento di Scienze della Terra, Pisa, Italia*
[3]*University of Melbourne, School of Geography, Australia*
[4]*Istituto di Geologia Ambientale e Geoingegneria (IGAG), Consiglio Nazionale delle Ricerche (CNR), Roma, Italia*
[5]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Pisa, Italia*

Keywords: Speleothems; Lacustrine carbonates; Stable isotopes

Continental carbonate successions (speleothems and lake sediments) from central Mediterranean are powerful archives of environmental variability. Assuming quasi-isotopic equilibrium precipitation, the stable oxygen isotope composition ($\delta^{18}O$) of these deposits is a proxy for that of the water from which they form, that in turn reflects -directly or indirectly- the $\delta^{18}O$ of the local meteoric precipitation ($\delta^{18}Op$). The $\delta^{18}Op$ results from changes in moisture source, condensation temperature, seasonality and precipitation amount, with the latter often considered as the predominant driver for carbonate $\delta^{18}O$ [e.g. Bard et al., 2002]. Other properties of the continental carbonates reflect instead environmental processes operating at the catchment-scale. These deposits thus offer the opportunity to create multiproxy records describing both local and regional climatic and environmental change. Here we present some examples of highly resolved, well-dated records from central Mediterranean caves and lakes covering past interglacial periods over the late Quaternary. The observed $\delta^{18}O$ variability indicates coherent patterns of hydrological variability during the investigated periods. The environmental evolution inferred by other proxies supports the interpretation of the $\delta^{18}O$. The reconstructed variability can also be tracked in marine records from the North-Atlantic, shedding lights on the links between Mediterranean precipitation variability and oceanic and atmospheric changes occurring at extra-regional scale.

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Combining forced ventilation with suitable inner coatings to reduce indoor radon levels in a scale model room

Paola Tuccimei[1], Gianfranco Galli[2], Michele Soligo[1], Martina Mattia[1], Manuela Portaro[1], Alessandra Briganti[3]

[1]*Università degli Studi Roma Tre, Dipartimento di Scienze, Roma, Italia*

[2]*Istituto di Geofisica e Vulcanologia, Sezione di Sismologia e Tettonofisica, Roma, Italia*

[3]*Istituto di Geologia Ambientale e Geoingegneria (IGAG), Consiglio Nazionale delle Ricerche (CNR), Montelibretti, Italia*

Keywords: Indoor radon; Vico Volcano; Radon mitigation

In the frame of “Radon rEal time monitoring System and Proactive Indoor Remediation” (RESPIRE), a LIFE 2016 project funded by the European Commission, the contribution of building materials of volcanic origin to indoor radon concentration was investigated. A very porous ignimbrite “Tufo di Gallese from Vico volcano (central Italy), was used to construct a scale model room of 62 cm × 50 cm × 35 cm (inner length × width × height, respectively) to study the effects of inner and outer coatings on radon levels [Lucchetti et al., 2020]. The combined influence of forced ventilation at different flow rates was investigated, too.

Experiments showed that outer covers (plastic films) promote the accumulation of indoor radon, reducing the air exchange trough the chamber walls, while inner covers (panels of painted plasterboard) are very effective to cut ^{220}Rn (thoron) levels, but less efficient for ^{222}Rn (radon).

Outdoor air introduction in the model room enhanced the barrier effect of inner covers, showing a direct correlation between air flow velocity and radon decrease. On the other hand, indoor air extraction was less successful than air introduction in reducing radon activity concentrations.

Final experiments were carried out without any coatings to evaluate the effect of ventilation (air introduction and extraction) alone. These tests were modelled with a modified version of Fick’s second law to describe the diffusion of radon gas through the chamber walls.

These results suggest that the combined use of suitable coatings on the inner walls of a building and outdoor air introduction at adequate rates are a good strategy for addressing radon mitigation actions.

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SESSION 4 - FLUID GEOCHEMISTRY IN VOLCANIC, GEOTHERMAL AND SEISMIC AREAS

Conveners:
Francesco Frondini (Università degli Studi di Perugia), Kyriaki Daskalopoulou (GFZ),
Giancarlo Tamburello (INGV)

Figure caption: Sulphur Efflorescence, Fossa Crater, Vulcano (Sicily), April 2022. Photo by Sergio Calabrese

Volcanic gas constraints on Carbon concentrations in, and outfluxing from, the Earth's upper mantle

Alessandro Aiuppa

Università di Palermo, Dipartimento di Scienze della Terra e del Mare, Palermo, Italia

Keywords: Volcanic gases; DECADE project; Continental rift magma

Volcanic gases bring key information on the volatile-rich nature of our planet interior, and are instrumental to better understanding cycling of volatiles in and out the Earth's mantle. Carbon is an essential element for life and its natural outgassing/ingassing through volcanism/subduction is though to have acted as a primary regulator of global climate in the pre-industrial era, and over geological timescales. In spite of several decades of enduring efforts, however, the global volcanic Carbon budget is only inaccurately understood. This contribution aims at reviewing some recent progresses made in the global Carbon flux inventory from subaerial volcanism, mostly arising from the DECADE project of the Deep Carbon Observatory (https://deepcarboncycle.org/home-decade) [Aiuppa et al., 2019; Fischer et al., 2019; Fischer et al., 2020]. Some key results of DECADE will be reviewed, including (i) an improved estimate of the CO_2 flux from the Earth's most actively degassing volcanoes, and (ii) a preliminary estimate of the total CO_2 flux from subaerial volcanism. A key conclusion that arises is that diffuse degassing through volcanic and tectonic areas is likely to represent the largest piece in the puzzle of global Carbon emissions from the Earth's mantle, and that such degassing is likely to concentrate in continental rift context. I will then review some recent volcanic gas work in which an attempt is made to understand the causes for the unusual Carbon enrichment in continental rift magma and gases (the C content of Oceanic Island Basalts, and their released gases will be tackled, too). This work brings profound implications for estimating the Carbon content of the Earth's upper mantle [Aiuppa et al., 2021]. Our novel volcanic gas results suggest, in particular, that Carbon may be increasing downward (with depth of melting) in the Earth's upper mantle, and that the average upper mantle Carbon content may be as high as ~350 ppm.

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Geochemical modelling of hydrothermal alteration at the San Vito Area of the Campi Flegrei geothermal system

Barbara Cantucci[1], Monica Piochi[2], Giordano Montegrossi[3,4]

[1]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Sismologia e Tettonofisica, Roma, Italia*
[2]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano, Napoli, Italia*
[3]*CNR-IGG, Istituto di Geoscienze e Georisorse, Firenze, Italia*
[4]*INSTM, Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Firenze, Italia*

Keywords: San Vito 1 well; TOUGHREACT V2.1 code; Campi Flegrei geothermal system (southern Italy)

The Campi Flegrei (CF) geothermal system sets in one of the most hazardous and studied caldera in the world. However, geochemical effects of fluid-rock interaction into the hydrothermal circulation were not properly considered in numerical models. In the framework of the long-term project, aimed to perform reactive transport simulations at CF, the objective of this study is to define mineralogical dataset and calibrate the thermodynamic model with actual data to be used as input for numerical simulations. The area drilled by the San Vito 1 well was selected as a case study. To achieve this goal, we carried out: 1) a review of available data and new petrographic analyses of cores, 2) the implementation and calibration of thermodynamic and kinetic dataset, 3) a 0D-geochemical model of the Campanian Ignimbrite formation, the most important deposits in the case study area. Batch-reaction simulations were performed considering variable PCO_2 at high (165 °C) and low (85 °C) temperatures by means of the TOUGHREACT V2.1 code [Xu et al., 2012] with the EOS2 module. The built geochemical model and thermodynamic dataset were then validated by results comparison with water sampled at the Tennis Hotel, considered the most representative of the shallow hydrothermal reservoir in the San Vito area [e.g. Aiuppa et al., 2006]. The built model correctly reproduced the alteration of primary minerals and precipitation of zeolites and clay, although some discrepancies were present. Simulations suggest that the observed mineral alteration is due to the fluid-rock interaction with PCO_2 ranging from 1.2 and 0.4-0.3 bars. Moreover, the simulated aqueous concentrations best matched the Tennis Hotel values within 10 years of simulation, hinting that geochemical reactions and fluid circulation toward the surface are quite fast as confirmed also by the high gas flows sampled at fumaroles [Tamburello et al., 2019] and from soil exhalation [Chiodini et al., 2010].

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The MaGa web-based database for the improvement of the knowledge about global CO_2 emissions from volcanoes diffuse degassing

Carlo Cardellini[1,2], Giovanni Chiodini[2], Alessandro Frigeri[3], Emanuela Bagnato[4], Francesco Frondini[1], Lisa Ricci[1], Artur Ionescu[5,1], Alessandro Aiuppa[6], Walter D'Alessandro[7]

[1]*Dipartimento di Fisisca e Geologia, Università di Perugia, Perugia, Italia*

[2]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Bologna, Italia*

[3]*Istituto di Astrofisica e Planetologia Spaziali, INAF, Roma, Italia*

[4]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano, Napoli, Italia*

[5]*Universitatea Babeș-Bolyai, Facultatea de Biologie și Geologie, Depatamentul de Geologie, Cluj-Napoca, România*

[6]*Dipartimento DisTeM, Università di Palermo, Palermo, Italia*

[7]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italia*

Keywords: MaGa web-based database; Gas emission; Diffuse CO_2 flux

Understanding the complex process of gas release from the Earth's interior by volcanoes and tectonically active areas, and improving the current estimates of global carbon emissions requires the access to data collections and tools to explore and analyse data. The Mapping Gas Emission (MaGa) web-based framework has been developed to collect and share measurements of gas compositions and fluxes from volcanic and tectonic gas emissions. The backend of MaGa stores the data into a spatially referenced relational database system, and standardized web services provide access to the geospatially enabled data for the analysis. MaGa currently contains the location of about 1000 gas emission sites (volcanic plumes, fumaroles, vents and diffuse degassing areas) and about 2000 records including gas flux and gas composition data from about 158 volcanoes. MaGa dataset on diffuse CO_2 degassing includes data from more than 200 degassing areas located in 101 volcanoes, that were investigated with more than 500,000 individual measurements of diffuse CO_2 flux. MaGa dataset has been elaborated in order to improve the estimate of the contribution of diffuse emission to the volcanic CO_2 focussing on the definition of the "typical" CO_2 emission from a diffuse degassing structure. This, coupled with the number of degassing volcanoes, was used to estimate the global CO_2 diffuse emission. Our results show that diffuse CO_2 degassing significantly contributes to the global volcanic CO_2 emission. Moreover, data analysis highlights that adequate sampling strategy and design, together with a reliable characterization of the deep CO_2 contribution to the total CO_2 flux, are fundamental to improve the estimate and reduce the uncertainties.

Geochemical and isotopic characterization of the groundwaters in the Mugello Basin (Tuscany, Central Italy) and possible insights into earthquake forecast

Lorenzo Chemeri[1], Orlando Vaselli[2,3], Franco Tassi[2,3], Jacopo Cabassi[3], Francesco Capecchiacci[2,3], Marta Lazzaroni[2,3], Andrea L. Rizzo[4], Fausto Grassa[4]

[1]Università degli Studi di Urbino, Dipartimento di Scienze Pure e Applicate, Urbino, Italia
[2]Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia
[3]CNR-IGG Istituto di Geoscienze e Georisorse, Firenze, Italia
[4]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italia

Keywords: Groundwater geochemistry; Stable isotopes; Mugello Basin (central Italy)

The Mugello Basin (MB) is an intermountain Pleistocene basin located 30 km north of Florence (Tuscany, Central Italy), which shows high seismicity with few events being characterized by $M_w \geq 6.0$, e.g. the June 29, 1919 Vicchio earthquake (M_w=6.2) that caused almost 100 fatalities and more than 400 injuries. The aim of this study was to characterize the geochemical and isotopic composition of groundwaters discharging from the MB to (i) identify the main geochemical processes, (ii) assess the possible interplay between deep-originated fluids and shallow aquifers and (iii) evaluate the use of geochemical parameters as seismic precursors. The waters were classified into two groups (a) calcium-bicarbonate, that include most samples, and (b) sodium-bicarbonate, where the occurrence of relatively high contents of sulfate, reduced S-bearing ions and F, Li and B was recognized. The Ca-HCO_3 waters were characterized by a slightly alkaline pH (below 8.3) and positive Eh values (150-200 meV), whereas the second group was dominated by alkaline pH (above 8.5) and negative Eh values (<-180 meV). The Ca-HCO_3 waters showed a N_2-dominated dissolved gas phase in contrast with the Na-HCO_3 waters that were enriched in CO_2 and CH_4. The geochemistry of the Ca-HCO_3 waters was mainly controlled by congruent dissolution processes involving carbonate-bearing rocks, whereas the Na-HCO_3 waters likely resulted by long-lasting water-silicate rock interactions. The inorganic dissolved gases were originated by the dissolution of atmospheric gas, as supported by the $^3He/^4He$ and $^{40}Ar/^{36}Ar$ isotopic ratios, with no evidence of inputs from deep fluids. Contrarily, the $\delta^{13}C$-CO_2 and $\delta^{13}C$-CH_4 values indicated a predominant biogenic production and the influence of secondary processes (e.g. methane oxidation in the shallow environment and carbon dioxide consumption). Therefore, the isotopic signatures of CO_2, CH_4 and He along with the main and trace element chemistry might be reliable seismic tracers for MB.

SESSION 4 - Fluid Geochemistry in Volcanic, Geothermal and Seismic Areas

Geochemical monitoring in seismically active areas in southern Apennine (Italy) in the framework of FURTHER project: first results

Daniele Cinti[1], Carlo Cardellini[2,3], Giovanni Chiodini[3], Andrea Gasparini[1], Luca Pizzino[1], Alessandra Sciarra[1], Nunzia Voltattorni[1], Carmine Apollaro[4], Giovanni Vespasiano[4], Antonella Deonofrio[4]

[1]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Sismologia e Tettonofisica, Roma, Italia*

[2]*Università degli Studi di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italia*

[3]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Bologna, Italia*

[4]*Università della Calabria, Dipartimento DIBEST (Biologia, Ecologia e Scienze della Terra), Arcavacata di Rende, Italia*

Keywords: FURTHER project; Geochemical monitoring; Southern Apennines (Italy)

In the frame of INGV's Departmental Project FURTHER, a multidisciplinary study devoted to establish the role of fluids in the preparatory phase of earthquakes, we are performing a geochemical monitoring in three target areas located in southern Italy. The selected areas (the Sannio-Matese and Pollino mountain ranges and the Mefite d'Ansanto degassing area) are located in seismically active sectors of southern Apennines where CO_2 earth degassing, from both soils and cold-to-thermal waters, occurs. In the Sannio-Matese and Pollino areas the discrete (seasonal) monitoring of chemical and isotopic composition, to quantify the "tectonic" CO_2 degassing from springs [Chiodini et al., 2020], is ongoing on selected sites. Springs emerging from carbonate aquifers and characterized by large discharges were selected on the basis of Total Dissolved Inorganic Carbon (TDIC) content and carbon isotopic composition ($\delta^{13}C_{TDIC}$). Here we present the first results of the discrete monitoring that will be integrated with the continuous monitoring of some selected parameters (i.e., temperature, electrical conductivity and water level) performed by multi-parametric sensors. The Mefite d'Ansanto area, which probably hosts the largest emission of non-volcanic CO_2 in the earth, quantified in ~2000 ton/day by Chiodini et al. [2010], will be investigated by a multi-parametric monitoring station for the continuous acquisition of air temperature, wind speed and direction and CO_2 concentration along vertical profiles in a cross-section of the channel, normal to the flow direction, where the gas emerging from the main emission is conveyed following the local topography.

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Hydrogeochemical and isotopic studies of groundwater in the Contursi area (southern Apennines)

Francesca Gori[1], Dario Buttitta[2,3], Marino Domenico Barberio[1], Maurizio Barbieri[1], Antonio Caracausi[3], Michele Paternoster[2,3] Marco Petitta[1]

[1]Università di Roma, La Sapienza, Dipartimento di Scienze della Terra, Roma, Italia
[2]Università degli Studi della Basilicata, Dipartimento di Scienze, Potenza, Italia
[3]Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italia

Keywords: Water geochemistry; Stable isotopes; Contursi (southern Italy)

Expanding knowledge on the origin and mixing of deep fluids and water-rock interaction processes in aquifers can provide crucial elements to the comprehension of crustal deformation processes. To deepen our understanding of deep fluid circulation and mixing in large regional aquifers, we performed a geochemical study of 25 springs in the Contursi area using measurements of chemical-physical parameters, major, minor and trace elements and stable isotopes. We identified three groups of springs (cold, hypothermal, and thermal type) based on the temperature values. The cold springs are mostly located at the eastern slope of Mt. Polveracchio, which represent the main recharge zone, and they are characterized by alkaline earth-bicarbonate hydrofacies. Instead, hypothermal and thermal springs, situated in the plain's inner zone, gradually show a hydrogeochemical evolution towards Na-Cl hydrofacies with the highest salinity value. Cold water chemistry is related to carbonate rocks (calcite and dolomite)-water interaction. In contrast, an additional contribution from evaporitic rocks cannot be excluded for the hypothermal and thermal water, as supported by saturation indices values (gypsum and anhydrite). The $\delta^{18}O$-δD values indicate a meteoric origin with a possible recharge from fractured carbonate rocks bordering the plain. Thermal fluids are closely related to the presence of tectonic discontinuities that constitute the pathways for the uprising fluids. We propose a hydrogeological circulation model according to which percolating groundwater circulates at a specific depth by following topographic gradients, and then reaches greater temperatures interacting with saline deep-seated thermal fluids. The study highlights the criteria to identify the most suitable sites for monitoring changes in hydrogeochemistry due to deep fluids uprising modulated by fault activity, to be further correlated with crustal deformation and possibly with seismicity.

Tectonically controlled volcanic degassing in the Eastern Carpathians, highlighted by geochemical characterization of mineral waters

Artur Ionescu[1,2,3,4], Antonio Caracausi[5], Orlando Vaselli[6], Kyriaki Daskalopoulou[7,8], Carlo Cardellini[2], Ferenc-Lazar Forray[1], Boglarka-Mercedesz Kis[1,9], Sergio Calabrese[5,10], Franco Tassi[6], Giovanni Chiodini[11], László Palcsu[3]

[1]*Universitatea Babeș-Bolyai, Facultatea de Biologie și Geologie, Departamentul de Geologie, Cluj-Napoca, România*

[2]*Università di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italia*

[3]*Nemzetközi Radiokarbion AMS Kompetencia és Kepzési (INTERACT) Központ, Debrecen, Magyarország*

[4]*Universitatea Babeș-Bolyai, Institutul de Cercetări pentru Sustenabilitate şi Managementul Dezastrelor bazate pe Calcul de Înaltă Performanţă (ISUMADECIP), Cluj-Napoca, România*

[5]*Istituto Nazionale Di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italia*

[6]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia*

[7]*Universität Potsdam, Institut für Geowissenschaften, Potsdam, Deutschland*

[8]*GeoForschungs Zentrum, Erdbeben- und Vulkanphysik, Potsdam, Deutschland*

[9]*MTA-ELTE Vulkanológiai Kutatócsoport, Budapest, Magyarország*

[10]*Università degli Studi di Palermo, Dipartimento Scienze della Terra e del Mare, Palermo, Italia*

[11]*Istituto Nazionale Di Geofisica e Vulcanologia, Sezione di Bologna, Bologna, Italia*

Keywords: CO_2 earth degassing; Water geochemistry; Eastern Carpathians (Romania)

Carbon or CO_2 earth degassing is a combined action produced by two distinct sources: a “punctual” contribution released from active volcanoes and a more regionally “diffuse” input from tectonically active areas. The deeply derived CO_2 from tectonically active areas is still matter of quantification although it may represent a significant source to CO_2 Earth degassing. Several studies highlighted that CO_2 from tectonically active areas is dissolved in the groundwaters circulating in large regional aquifers. The Eastern-Carpathians Volcanic Range (ECVR) embraces a large chronological period, spanning from millions to tens of thousands of years. Although ECVR is not a volcanically active area, it is considered as one of the highest CO_2 volcanic degassing regions in Eastern Europe. Close to the south-eastern portion of EVCR, there is one of the most seismic areas in Europe: the Vrancea region, where strong earthquakes (hypocentral depth 60-220 km) repeatedly occurred in recent times (e.g. 1940 and 1977). The seismogenic structure is envisaged as a narrow high-seismic body embedded in the upper mantle, likely related to subduction processes in the Eastern Carpathians. Starting from these two facts, in the framework of a Deep Carbon Observatory (DCO) supported project, entitled “Discovering the Carpathian Volcanism”, mineral springs from the Eastern Carpathians were sampled along a NW-SE transect. Water chemistry and isotopes and carbon-13 from TDIC were analysed for 102 samples and a large database, based on the literature data of source water discharges, was created. Based on the new results and the compiled database (> 1600 data entries), this work is aimed at i) producing a regional degassing map for the Eastern Carpathians; ii) quantifying the carbon transported through the main groundwater systems; iii) computing the subsurface reservoir temperatures, iv) assessing whether the volcanic carbon as diffuse source is actively controlled by the tectonic setting.

Fluids flow path in the Los Humeros Geothermal Field: inference from geochemical surveys

Matteo Lelli[1], Thomas Gunter Kretzschmar[2], Jacopo Cabassi[3], Marco Doveri[1], Juan Ignacio Sanchez-Avila[4], Fabrizio Gherardi[1], Gabriella Magro[1], Francesco Norelli[1]

[1]*Istituto di Geoscienze e Georisorse, CNR, Pisa, Italia*
[2]*Center for Scientific Research and Higher Education, Ensenada, B.C., Mexico*
[3]*Istituto di Geoscienze e Georisorse, CNR, Firenze, Italia*
[4]*CeMM Research Center for Molecular Medicine, Wien, Austria*

Keywords: Fluid geochemistry; Stable isotopes; Los Humeros Geothermal Field (Mexico)

Geothermal power in Mexico is mainly produced in four geothermal fields operated by the Comision Federal de Electricidad (CFE), and the Los Humeros Geothermal Field (LHGF) is ranked third in terms of generated capacity (up to 95.0 MW). The development of any geothermal project must start from the knowledge of the conceptual model of the natural system, focusing in particular on: recharge mechanisms, feeding zones, fluid flow-path, temperatures at the productive level and secondary processes (i.e. phase separation, phase segregation). Productive levels in the LHGF are mainly located in the andesite and basalt layers, which are buried by low-permeable Quaternary ignimbrite, while the bottom is composed of limestone rocks, outcropping on the west side of the field and constituting the Sierra Madre Oriental ridge.In the framework of the Gemex project (H2020 - EU), detailed fluid geochemical surveys were carried out in June 2017 and March 2018, during which 57 and 87 samples were respectively collected, involving cold and thermal springs, water wells and maar lakes located around and inside the LHGF. Samples from fumaroles inside the producing area were also collected for the first time, together with fluids from re-injection wells.

Chemical and isotopic (δD and $\delta^{18}O$) data confirm the presence of a meteoric component. Its contribution in terms of recharge may be higher than previously assumed, even if minor contribution from deep hot acidic fluids cannot be ruled out. Starting from the experimental data for natural gas emissions (fumarolic condensates) and geothermal fluids from wells, the evolution of isotopic values in the liquid-rock-steam system during water-rock interaction and phase separation processes was modelled. The isotopic composition for the infiltration water obtained by the model is similar to that observed in cold springs located in the Sierra Madre Oriental, suggesting limestone outcrops on the west sector of the LHGF as probable feeding zone.

Carbon degassing through karst hydrosystems of Greece

Lorenza Li Vigni[1], Kyriaki Daskalopoulou[2,3], Sergio Calabrese[1,4], Francesco Parello[1], Carlo Cardellini[5,6], Stefano Caliro[7], Giovanni Chiodini[6], Walter D'Alessandro[4]

[1]*Università degli Studi di Palermo, Dipartimento delle Scienze della Terra e del Mare, Palermo, Italia*
[2]*University of Potsdam, Institute of Geosciences, Potsdam Golm, Deutschland*
[3]*GFZ German Research Centre for Geosciences, Potsdam, Deutschland*
[4]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italia*
[5]*Università degli Studi di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italia*
[6]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Bologna, Italia*
[7]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano, Napoli, Italia*

Keywords: CO_2 degassing; Karst spring geochemistry; Greece

Estimation of CO_2 degassing from active tectonic structures and regional hydrothermal systems is essential for the quantification of present-day Earth degassing [Frondini et al., 2019 and references therein]. Due to the high solubility of CO_2 in water, great amounts of deep inorganic carbon can be dissolved, transported, and released from regional aquifers. By applying a mass-balance approach [Chiodini et al., 2000], different sources of the dissolved CO_2 can be discriminated. The main source of degassing in Greece is concentrated in hydrothermal and volcanic areas. However, deep CO_2 from active tectonic areas has not yet been quantified. A key point of this research is to investigate the possible deep CO_2 degassing through the big karst aquifers of Greece. From May 2016, 156 karst springs were sampled along the greatest part of the Hellenic region. To discriminate the different carbon sources, we analyzed the chemical and isotopic composition of total dissolved inorganic carbon (TDIC). Results yield TDIC values from 1.89 to 21.7 mmol/l and $\delta^{13}C_{TDIC}$ from -16.61 to -0.91 ‰. On this basis, karst springs are clustered into two groups: (a) low TDIC and $\delta^{13}C_{TDIC}$ values and (b) intermediate TDIC and $\delta^{13}C_{TDIC}$ values. The carbon of the first group derives from organic source and dissolution of carbonates; whilst the second group shows a possible carbon input from deep source. This geogenic carbon is mostly related to high heat flux areas, often near active or recent (Quaternary) volcanic systems.

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Element volatilization during lava lake degassing as inferred from acid rain

Marcello Liotta

Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italia

Keywords: Acid rains; Trace elements; Nyiragongo and Masaya volcanoes

Volcanoes hosting lava lakes represent perfect natural sites where scientists can collect samples to improve the understanding of geochemical processes taking place at the lava-atmosphere interface. Volcanogenic elements are released into the atmosphere from the continuously degassing of lava lakes. The emissions resulting from volcanic plumes include solid particles, acidic droplets, and gaseous species. The emitted gases and particles also influence the chemical composition of precipitation. Interaction processes between volcanic plumes and falling raindrops leave clear signatures in water and provide the opportunity to retrieve useful information on volcanic emissions as well as to evaluate their environmental impact. Recent papers [Liotta et al., 2017; Liotta et al., 2021] investigated the chemical composition of single rain events at Nyiragongo volcano (Democratic Republic of Congo) and at Masaya volcano (Nicaragua) to obtain information on the mobility of plume-derived volcanogenic elements and on their relative volatility. Findings from both the volcanoes showed that the most acidic gases readily dissolve in water, and so their ratio in rain samples reflects that of the volcanic plume. SO_2 requires time to be oxidized to H_2SO_4, which is easily dissociated in water. The transport of HF is mediated by the large amount of silicate particles generated at the lava-air interface. The refractory elements dissolved in rain samples derive from the dissolution of silicate particles, and most of them (Al, Mg, Ca, Fe, Be, Ti, Mn, and Sr) are present at exactly the same molar ratios as in the rocks as well as rare earth elements (REEs). By contrast, Li, Na, K, Cr, Ni, Cu, Zn, Rb, Cd, Sb, Te, Cs, Tl, Pb, and Bi are enriched relative to the whole-rock composition, suggesting that they are volatilized during magma degassing. The comparison between several volcanoes on the Pb emissions highlights the effect of oxygen fugacity in determining its volatility.

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Modeling of fluid-rock interaction processes at White Island (NZ)

Giordano Montegrossi[1,2], Federica Meloni[2,3], Bruce Christenson[4]

[1]CNR-IGG, Istituto di Geoscienze e Georisorse, Firenze, Italia

[2]INSTM - Interuniversity Consortium, Firenze, Italia

[3]Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia

[4]National Isotope Centre, GNS Science, Lower Hutt, New Zealand

Keywords: Chemical reaction model; TOUGHREACT V2.1; White Island (New Zealand)

A necessary step to creating a reactive transport model for the White Island (NZ) volcano, is the calibration of a chemical reaction model. The model should be able to reproduce the main geochemical processes occurring in the acidic springs, shallow ephemeral lake and groundwater. White Island (WI) is an active composite stratovolcano situated some 40 km north of the Bay of Plenty coastline, New Zealand, where it is present a vigorous magmatic-hydrothermal system continuously operating and studied for decades. The modelling code used is the Toughreact v2.1 with the EOS2 equation [Xu et al., 2012], with the thermodynamic database Thermoddem [Blanc et al., 2012]. The models consist of batch reaction model (single cell) in which we can add cooling and evaporation. The source components needed to model the WI hydrothermal system were defined according to the findings in Christenson et al., 2017, and are: i) meteoric water, ii) magmatic fluid (as CO_2, H_2S, SO_2, HCl), iii) local NZ seawater and iv) volcanic Glass [Cole et al. 2001]. The WI volcanic glass was added to the database according to the procedure described in Aradóttir et al., [2012] and Piochi et al., [2021]. The processes needed to reproduce the analytical dataset are: i) interaction glass-sea water, ii) interaction glass-meteoric water, iii) interaction magmatic fluid-glass-sea water, iv) interaction magmatic fluid-glass-meteoric water, v) scrubbing of the magmatic fluid, vi) evaporation and vii) the presence of brine or connate water, needed to account for an excess of Mg and Cl in the water analysis with respect to the seawater composition. The results of the batch simulations show that we are able to reproduce all fluid compositions reported in Christenson et al., [2017] using only these four attributed endmembers.

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Simulations of volcanic outgassing and volatile chemical speciation for investigating the atmospheres of rocky planets

Gianluigi Ortenzi[1,2], Frank Sohl[1] and Lena Noack[2]

[1]German Aerospace Center, Institute of Planetary Research, Berlin, Deutschland
[2]Freie Universitaet Berlin, Department of Earth Sciences, Berlin, Deutschland

Keywords: Volcanic outgassing; Melt volatile partitioning; Rocky planet atmospheres

Volatiles represent the perfect link between the interior and the atmosphere of a planet and the volcanic outgassing is a central process for investigating the composition and the evolution of rocky planet atmospheres. By applying a multidisciplinary approach, we simulate the volatile transition from the mantle to the atmosphere considering the melt volatile partitioning, the gas chemical speciation for the C-O-H system and the composition of the corresponding outgassed atmospheres. We show how the mantle redox state influences the final outgassed composition. Starting with the simulation of the mantle convection and the melt production [Noack et al., 2017, Dorn et al., 2018], the mantle redox state affects the volatile partitioning between the mantle and the melt. In reducing conditions, the carbonate partitioning between the mantle and the magma is inhibited [Grott et al., 2011] producing silicate melts depleted in carbon species and enriched in H_2O and H_2. Once the melt reaches the surface, we simulate the volatile chemical speciation and the volcanic outgassing [Holloway 1981, Fegley 2013, Gaillard and Scaillet 2014, Schaefer and Fegley 2017]. In reducing conditions, the volatile composition is dominated by H_2 and by a small portion of H_2O and CO_2 whereas, in oxidising scenarios the outgassed species are H_2O and CO_2 [Ortenzi et al., 2020, Guimond et al., 2021]. Finally, the outgassed composition affects the atmospheric pressure and radial extent. We show that reducing scenarios generate larger atmospheric thickness and lower pressure at surface compared to oxidised conditions. Atmosphere predictions are a useful tool for investigating the atmospheric evolution and for interpreting the observations of rocky planet atmospheres.

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Crustal vs mantle degassing in the High Agri Valley (southern Italy): new evidences from an old borehole of hydrocarbon exploitation

Michele Paternoster[1,2], Dario Buttitta[1,2], Serena Panebianco[1,3], Antonio Caracausi[2]

[1]*Università degli Studi della Basilicata, Dipartimento di Scienze, Potenza, Italia*

[2]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italia*

[3]*Consiglio Nazionale delle Ricerche, Istituto di Metodologie per l'Analisi Ambientale (CNR-IMAA), Potenza, Italia*

Keywords: Fluid geochemistry; Stable isotopes; Tramutola well (southern Italy)

The High Agri Valley (HAV) is an inter-montane basin of the southern Apennine chain characterized by complex geological setting and active tectonics. This area also hosts the largest onshore Western European oil field. In this work, we focused on thermal water from Tramutola well (TRW), built by ENI, with the occurrence of bubbling gases. TRW water is hot (28°C) and belong to Na-HCO_3 hydrofacies. The gaseous species were collected in order to measure the abundances and C-He isotope ratios, excellent geochemical tracers to discriminate the natural sources (crustal, mantle and atmospheric) and to define CH_4 and CO_2 output. Unlike HAV groundwater, TRW gases are CH_4-dominated (82%), CO_2 is up to 1.92%, O_2 and N_2 up to 0.06% and 12.8 % respectively. The ^{4}He/^{20}Ne ratio in the collected gases is three orders of magnitude higher than air-one (0.318), highlighting that atmospheric contribution is negligible. Helium isotope (^{3}He/^{4}He, expressed as R/Ra) indicate a prevalent radiogenic component with a contribution of mantle-derived helium (~20%). The δ^{13}C-CO_2 value is of -3.5‰ VPDB, consistent with a mantle origin. TRW gases have low CO_2/^{3}He ratios compared to mantle carbon end-member, probably due to secondary processes such as calcite precipitation. Methane isotope composition indicates a likely microbial isotopic signature (δ^{13}C-CH_4 =−63.1‰ δD−CH_4=−196‰), probably due to either (1) biodegradation processes of thermogenic hydrocarbons, earlier generated by thermocracking process or (2) ongoing microbial methanogenesis in the shallow organic rich clays hosting the gas. The methane output, evaluated by means of anemometric measurement of the volume flow (m^3/h) and flow velocity (m/s), is ~156 t/y, which represent about 1.5% of total national anthropogenic sources related to the fossil fuel industry [Etiope et al., 2007]. The measured CO_2 output (3.2 ton/y) is from 2 to 5 orders of magnitude lower than the budget of mantle-derived CO_2 from Italian volcanoes.

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Geochemical monitoring in both cold and thermal aquifers in the Irpinia region (southern Apennines): first results from the INGV project "Myburp"

Luca Pizzino[1], Daniele Cinti[1], Fausto Grassa[2], Alessandra Sciarra[1]

[1]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Sismologia e Tettonofisica, Roma, Italia*
[2]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italia*

Keywords: Myburp project; Water geochemistry; Southern Apennines

The study of geochemical transients in groundwater associated with seismicity needs long time series of observations for answering the main questions regarding the role of fluids in the earthquake preparing phases [e.g. Chiodini et al., 2020; Gori and Barberio, 2021 and references therein]. Generally, these studies are not homogeneously performed during the seismic cycle, but are diffusely carried out in the co- and immediately post-seismic phase (until months later) while, in the pre-seismic phase, a systematic acquisition of geochemical parameters is more sporadic. This could hamper a deep understanding of the chemical and physical processes occurring at depth, as well as to define and model the groundwater-earthquake relationship. In light of the above, since April 2021, a multidisciplinary INGV project named "Myburp" is currently ongoing in the Irpinia area (southern Italy), repeatedly hit by large earthquakes (up to M=7) in the last centuries. The sites selected for monthly samplings are: *i*) the largest cold springs of Caposele and Cassano Irpino (both tapped by the Pugliese aqueduct), issuing from the karst hydrostructure of the Picentini Mts. and *ii*) two CO_2-rich thermal-mineral aquifers, located in the upper Sele river valley (Capasso site) and in the Ansanto valley (San Teodoro site, north-eastern Irpinia). The chemistry of cold and thermal waters is dominated by Ca, Mg and HCO_3, with remarkable differences in the physical-chemical parameters, ionic abundance, minor and trace elements, dissolved gas content and isotopic composition between them. Cold waters have discharge temperature in the range 9-11°C, alkaline pH (7.7-8.2) and low salinity (290-380 µS/cm), while thermal waters show temperatures between 26 and 48°C, slight acidic pH (6.4-6.6) and medium to high salt content (1.3-6.6 mS/cm). $\delta^{13}C_{TDIC}$ point out a prevalent organic origin of CO_2 in the cold aquifers, while thermal waters likely transport large amounts of deeply derived CO_2.

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SESSION 4 - Fluid Geochemistry in Volcanic, Geothermal and Seismic Area

Active degassing of deep-sourced fluids in central western Europe: new evidences from a geochemical study in Serbia

Paolo Randazzo[1], Antonio Caracausi[2], Alessandro Aiuppa[1], Carlo Cardellini[3,4], Giovanni Chiodini[4], Walter D'Alessandro[2], Lorenza Li Vigni[1], Peter Papic[5], Goran Marinkovic[6], Arthur Ionescu[3,7,8]

[1]*Università di Palermo, Dipartimento di Scienze della Terra e del Mare, Palermo, Italia*
[2]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italia*
[3]*Universita degli studi di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italia*
[4]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Bologna, Italia*
[5]*University of Belgrade, Faculty of Mining and Geology, Beograd, Serbia*
[6]*Geological Survey of Serbia, Belgrade, Serbia,*
[7]*Universitatea Babeș-Bolyai, Facultatea de Biologie și Geologie, Depatamentul de Geologie, Cluj-Napoca, România*
[8]*International Radiocarbon AMS Competence and Training Center (INTERACT), Institute for Nuclear Research, Debrecen, Hungary*

Keywords: Fluid geochemistry; Stable isotopes; Serbia

Recognizing and identifying the transfer of mantle-derived fluids (e.g., CO_2, N_2, noble gases) in continental regions is critical for investigating the processes that shape the Earth's interior and for developing exploration strategies of natural resources (i.e. hydrocarbons, ore deposits, heat sources) [e.g. Broadley et al., 2020; Caracausi & Sulli, 2019; Chiodini et al., 2020; Byrne et al., 2017]. The outgassing of deep-mantle volatiles has recently been verified in many crustal segments, including western-central Europe [e.g., Brauer et al., 2013], but the geological/tectonic controls on deep fluid migration remain to be fully understood. Here, we report on the results of an extensive geochemical survey of gas manifestations in the Vardar zone (Serbia, Europe), a mega-suture zone between Eurasia and Africa plates. Based on their chemical compositions (C, He, Ne, Ar), the studied gases are clustered into three distinct groups (CO_2, N_2 and CH_4 dominated). The He isotope ratios, ranging from 0.08 to 1.19 Ra, identify a weak (<20 %) but persistent regional mantle-derived component, with the lowest $^3He/^4He$ values reflecting radiogenic He production from the nearby granitoid intrusions. The $\delta^{13}C$ values range from -20.2 to -0.1 ‰, with the more negative compositions being observed in N_2-dominated samples. The combined analysis of He and C(CO_2) abundances and isotopic composition demonstrates that the main processes controlling the chemistry of the outgassing volatiles are i) mixing between crustal and mantle-derived volatiles together with ii) the partial dissolution of volatiles in groundwater. Finally, we estimate the mantle He flux at 9.0×10^9 atoms m^{-2} s^{-1}, or up to 2 orders of magnitude higher than the typical fluxes in stable continental areas, suggesting a tectonic control of fluid migration through the crust.

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Equilibrium-kinetics interplay controls molecular hydrogen abundance and hydrogen isotope composition in hydrothermal fluids

Andrea Ricci[1], Barbara I. Kleine[1], Jens Fiebig[2], Jóhann Gunnarsson-Robin[1], Kennedy Mativo Kamunya[3], Bruce Mountain[4], Andri Stefánsson[1]

[1] *Institute of Earth Sciences, University of Iceland, Iceland*

[2] *Institute of Geosciences, Goethe University, Deutschland*

[3] *Kenya Electricity Generating Company Ltd., Olkaria Geothermal Project, Kenya*

[4] *GNS Science, Wairakei Research Centre, New Zealand*

Keywords: Hydrothermal fluids; Hydrogen; Geothermometry

Molecular hydrogen (H_2) is among the main components in hydrothermal fluids where it exerts a major role in geochemical and biological processes. Nevertheless, the understanding and quantification of factors controlling H_2 abundance and isotope systematics remain uncertain. Here, we present hydrogen fugacity (fH_2) and δD values of H_2 and H_2O in hydrothermal fluids from on-land hydrothermal systems worldwide (Greece, Iceland, Kenya and New Zealand), related to rift and arc settings and sourced by seawater and meteoric water. Comparison of the data with geochemical modeling results reveals that H_2 is predominantly sourced from the reduction of H_2O by oxidation of aqueous Fe^{+II} to Fe^{+III}. We argue that fH_2 in hydrothermal fluids is not fixed by a sole redox buffer but instead controlled by metastable mineral-fluid and fluid-fluid equilibria upon progressive rock alteration and depends on temperature, rock-to-water ratio (r/w), source water composition and volcanic gas input. Our data demonstrate that δD-H_2 values of reservoir fluids at depth are controlled by the δD-H_2O value and the equilibrium isotope fractionation at hydrothermal reservoir temperatures. Attainment of isotopic equilibrium at reservoir conditions is supported by fast isotopic equilibration times at $T > 200$ °C, on the order of minutes to few hours, relative to hydrothermal fluid residence times within the reservoirs of years to decades or even longer. Upon fluid ascent to surface, H_2-H_2O isotope re-equilibration may occur. For fast flowing well discharges, such isotope re-equilibration was observed to be negligible whereas slow-flowing fumarole gases in some cases show full re-equilibration at the sampling temperature. Based on the extent of hydrogen isotope disequilibrium, we estimate reservoir-to-surface travel times of minutes to <3 hours and a few hours to days for wells and fumarolic fluids, respectively.

Chemical and isotopic characterization of fluids circulating in the Massif Central (France) to investigate the regional degassing process

Lisa Ricci[1], Francesco Frondini[1], Daniele Morgavi[1], Guillaume Boudoire[2],
Mickael Laumonier[2], Stefano Caliro[3], Carlo Cardellini[1], Giovanni Chiodini[4]

[1]*Università di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italia*
[2]*Laboratoire Magmas et Volcans, UCA, CNRD, IRD, OPGC, Clermont-Ferrand, France*
[3]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano, Napoli, Italia*
[4]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Bologna, Italia*

Keywords: CO_2-rich hydrothermal system; Dissolved inorganic carbon; Massif Central (France)

The European Cenozoic Rift System (ECRIS) is a 1100 km long passive rift in Central Europe. A part of it, the French Massif Central, located in central-southern France, is characterized by the presence of deep CO_2-rich hydrothermal systems, studied since the middle ‘70s for geothermal purposes [Fournier et al., 1974]. The discharge of deep fluids at the surface occurs with the presence of bubbling pools, mofettes and numerous CO_2-rich springs (thermal and fresh) characterized by small flow rates and very high pCO_2. Despite the clear evidence of the ongoing degassing process, its characteristics and extension are still poorly studied and generally limited to small parts of the region [Gal et al., 2018]. The aim of our study is to describe the degassing process and quantify the amount of deep CO_2 discharged to the atmosphere at a regional scale. Here, we show some preliminary results based on the analysis of more than 100 samples, including chemical and isotopic composition of waters, isotopic composition of dissolved carbon and chemical composition of dissolved gases. δD and $\delta^{18}O$ values plot between the global meteoric water line and the regional meteoric water line [Fouillac et al., 1991], suggesting that both thermal and fresh waters are of meteoric origin; the $\delta^{18}O$-altitude relationship indicates that groundwater infiltrates at elevations between 800 and 1600 m, 1000 m a.s.l. in average. The isotopic composition of dissolved inorganic carbon (TDIC) and the composition of dissolved gases show that, after infiltration, a significant portion of circulating waters are strongly enriched in a deep CO_2-rich component of mantle origin. Before or immediately after the discharge from springs, most of the dissolved CO_2 is released into the atmosphere. A preliminary carbon mass and isotopic balance show that the degassing rate of Massif Central is about 10^6 mol km^{-2} yr^{-1}, of the same order of magnitude as the global baseline of geothermal areas (Kerrick et al., 1995).

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CO_2 budget of Furnas Lake, São Miguel Island, Azores: 3D chemical tomography of a degassing volcanic lake

Giancarlo Tamburello[1], Dmitri Rouwet[1], César Andrade[2,3], Fátima Viveiros[2,4], José Virgílio Cruz[2,4]

[1]*Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Bologna, Italia*
[2]*IVAR - Research Institute for Volcanology and Risks Assessment, University of the Azores, Ponta Delgada, Portugal*
[3]*CIVISA - Centre for Information and Seismovolcanic Surveillance of the Azores, University of the Azores, Ponta Delgada, Portugal*
[4]*FCT - Faculty of Sciences and Technology, University of the Azores, Ponta Delgada, Portugal*

Keywords: Dissolved CO_2 3D mapping; Volcanic lakes; Furnas Lake (São Miguel Island, Azores)

Volcanic CO_2-dominated gases can slowly accumulate at the bottom of volcanic lakes by dissolution processes. The most studied cases are Monoun and Nyos lakes (Cameroon), which in 1984 and 1986 violently released huge amounts of previously accumulated CO_2, killing approximately 37 and 1700 people respectively [Sigurdsson et al., 1987; Kusakabe et al., 2000]. These two disasters increased the general awareness of the potential danger this type of volcanic lake may represent and increased the number of studies and monitoring networks on volcanic lakes. The only way to monitor the accumulation of CO_2, or other gas species, in a volcanic lake is to lower Conductivity- Temperature-Depth/Pressure (CTD) probes, sample lake water and measure dissolved gases along vertical profiles. In most studies, these vertical profiles are performed only where the anomalous deep accumulation is known to occur whereas the lateral variability and extension are often unknown. Here, we report a 3D mapping of the dissolved CO_2 at Furnas Lake (São Miguel Island, Azores) obtained with a lightweight probe that uses infrared detection to measure the partial pressure of CO_2 gas dissolved in liquids [Rouwet et al., 2021]. We also used a multi-parametric probe to measure pH, ORP, conductivity, dissolved O_2, and temperature. The measurements allowed to interpolate the dissolved CO_2 at different depths and around the lake. We integrated the total amount of measured gas to obtain a total CO_2 mass of ~ 100 tons dissolved as $CO_{2\,(aq)}$. If we also consider the carbon dissolved as bicarbonate (HCO_3^- concentrations obtained from Cruz et al., 2006 and Andrade et al., 2016), we obtain a total CO_2 mass (CO_2 + HCO_3^-) ranging from 600-800 tons. Our result represents the first direct quantification of the total dissolved CO_2 in a volcanic lake, and the reported methodology opens new perspectives for volcanic lake monitoring and risk assessment.

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Measurements of CH4 fluxes from lakes: the case of Lake Astroni, Phlegraean Fields, southern Italy

Franco Tassi[1,2], Alice Repetto[1], Antonio Randazzo[1,2], Francesco Capecchiacci[1,2,3], Stefania Venturi[1,2], Jacopo Cabassi[2], Roberto Isaia[3], Stefano Caliro[3], Orlando Vaselli[1,2]

[1]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia*

[2]*Consiglio Nazionale delle Ricerche, Istituto di Geoscienze e Georisorse, Firenze, Italia*

[3]*Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Napoli, Osservatorio Vesuviano, Napoli, Italia*

Keywords: Wetlands; Fluid geochemistry; Lake Astroni (Phlegraean Fields, southern Italy)

Wetlands are well-known as significant sources of CH_4 to the atmosphere, whereas lakes are commonly considered as sinks for C-bearing volatiles produced within bottom sediments. In this work, we present the results of two surveys (summer 2020 and winter 2021, respectively) carried out at the 300×200 m wide Lake Astroni (Phlegraean Fields, southern Italy) to measure CH_4 and CO_2 diffusive fluxes (fCH_4 and fCO_2) from the lake surface. The fCH_4 and fCO_2 values, measured according to the floating chamber method, were compared to those computed according to water and dissolved gas chemical compositions. Both measured and computed data show that Lake Astroni is a significant CH_4 and CO_2 source to the atmosphere, with values of the same order of magnitude as those measured in highly-producing wetlands at this latitude. These results are quite surprising, considering that the depth of the lake (up to 5 m) is significantly higher than that of a typical wetland. Consistently, significant amounts of dissolved CH_4 and CO_2 were recognized at ≥1 m depths, where an anoxic hypolimnion occurs. According to the $d^{13}C\text{-}CH_4$ and $d^{13}C\text{-}CO_2$ values measured at the lake bottom, CH_4 is totally biogenic, whereas CO_2 is mostly of hydrothermal origin, as supported by the occurrence of hydrothermal gas emissions along the lake rim. Such a high CH_4 release to the atmosphere is likely depending on the combination of different factors: (i) a large availability of labile organic matter provided by the forest surrounding the lake; (ii) the external (hydrothermal) CO_2 source; (iii) the low exposure to wind due to the steep flanks of the Astroni caldera, preventing the vertical circulation of lake water and favoring the development of an anoxic layer. Microbiological analysis on lake water and sediment samples are planned to be carried out shortly to provide further insights into the biogeochemical processes at the origin of this extremely CH_4-rich environment.

Linking soil CO_2 emissions to the structural features of a fault: insights from the Monterotondo-Sasso Pisano area (Larderello geothermal field, Italy)

Marco Taussi[1], Barbara Nisi[2], Andrea Brogi[3,4], Domenico Liotta[3,4], Maddalena Perrini[3], Miller Zambrano[5], Martina Zucchi[3], Orlando Vaselli[2,6]

[1]*Università degli Studi di Urbino Carlo Bo, Dipartimento di Scienze Pure e Applicate, Urbino, Italia*
[2]*Consiglio Nazionale delle Ricerche, Istituto di Geoscienze e Georisorse, Firenze, Italia*
[3]*Università degli Studi di Bari "Aldo Moro", Dipartimento di Scienze della Terra e Geoambientali, Bari, Italia*
[4]*Consiglio Nazionale delle Ricerche, Istituto di Geoscienze e Georisorse, Pisa, Italia*
[5]*Università degi Studi di Camerino, Scuola di Scienze e Tecnologie (sezione di geologia), Camerino, Italia*
[6]*Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia*

Keywords: Diffuse CO_2 flux; Discrete Fracture Network modelling; Larderello geothermal system (central Italy)

Carbon dioxide (CO_2) emission naturally released from geothermal systems is a timely theme, being the object of scientific research for decades. Establishing the diffuse degassing processes and pathways provide valuable information for exploration and exploitation purposes of geothermal reservoirs. Areas with high CO_2 emissions are indeed able to reveal major upflow zones from deep reservoirs through deep-reaching permeable fault zones. In this work, a high-resolution (3 x 3 m grid) CO_2 flux (up to 2927 g m^{-2} d^{-1}) and soil temperature (up to 98.8 °C) survey was carried out in a selected area of the Monterotondo-Sasso Pisano fault zone (Larderello geothermal system, Tuscany, Italy) to define the architecture of the fault system and estimate the effective CO_2 emission from the fault zone. The presence of multiple populations of CO_2 flux, supported by the carbon isotopic content measured in the interstitial carbon dioxide, suggest that three different transport mechanisms control the emissions: i) purely diffusive, ii) mixed diffusive-advective, and iii) purely advective, characterized by efflux values of <20, between 20 and 300 and >300 g m^{-2} d^{-1}, respectively. The spatial distribution of these fluxes well agrees with the fracture distribution of Jurassic radiolarite (Diaspri Fm) dissected by NNE-striking faults. The interaction between fractures and faults enhances, locally, the secondary permeability of rocks as highlighted by the correlation between Discrete Fracture Network modelling and advective flux. Eventually, by normalizing the CO_2 output to the fault strip (1350 m^2), we came up with the released of CO_2 equal to ~155 t d^{-1} km^{-2}, although when the area characterized by advective flux (460 m^2) was considered the efflux rose up to 326 t d^{-1} km^{-2}, confirming the pivotal role of the structural features in controlling the fluid emissions.

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Istituto Nazionale di Geofisica e Vulcanologia
Via di Vigna Murata, 605
00143 Roma
tel. +39 06518601

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