

PLINIUS



Società Italiana di Mineralogia e Petrologia

c/o Dipartimento di Scienze della Terra

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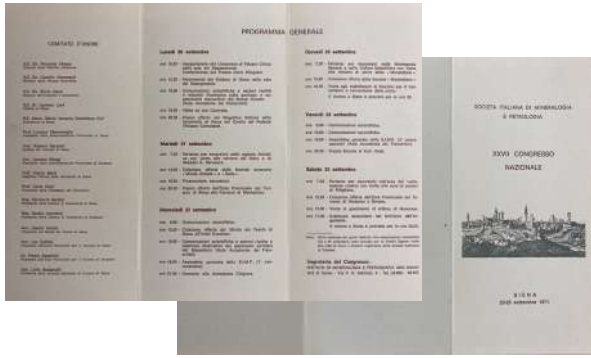
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FOTO COPERTINA: Silvia Favaro | L'Urlo di Munch

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SIMP COMMUNICATION



Meeting programs were like restaurant menu

A young Bernardo Carmina (bottom) working on the SIMP website (top)



Paleozoic



One of the first (top) and the last (bottom) used fax machines

From Paleozoic to Mesozoic = from Bernardo to Lorenza



Correcting mistakes was difficult with the fax

ACROSS GEOLOGICAL TIMESCALES

Restyling of the Plinius Editorial Board (current team)

MEET THE NEW EDITORIAL BOARD!



A new powerful tool for the storage and communication from the SIMP (CDs)



SIMP online upgrades



Plinius 49/2023 is online!



Lorenza Fascio and her SIMP job

SIMP on social networks!



...to be continued

Plinius Editorial Board UPDATED

MEET THE NEW EDITORIAL BOARD!

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From the Editorial Board

Dear Members,

The editorial transformation of our magazine continues to evolve. The beating heart of the magazine remains the sections dedicated to the Extended Abstracts of the Juniors SIMP's Ph.D., to which DOIs are assigned. However, it is now accompanied by new sections aimed at enhancing the cultural, educational, and dissemination activities involving the Society and its Members. These new sections include interviews with SIMP awardees and coverage of SIMP-sponsored activities, all framed within a new graphic design. Members will play an integral role in this transformation through the cover image contest!

To achieve these goals, the editorial board, originally composed of Concetta Rispoli, Nadia Malaspina, Lorenza Fascio, Virginia Marchionni, Stefania Corvò, Andrea Maffei, Maria Verde, and Alessandro Petroccia, has been expanded with the addition of two young SIMP members: Sara Nerone and Valeria Indelicato. We hope these new initiatives will invigorate our journal and, with the contribution of all Members, PLINIUS will continue to be a point of reference for those interested in the issues, research, and outreach activities in the fields of Mineralogical and Petrological Sciences.

Senior's Interviews

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Francesco Princivalle



Francesco Princivalle is a full professor of Mineralogy at the University of Trieste (Department of Mathematics and Earth Sciences) since November 2001.

He has held the position of Director of the Department (Earth Sciences, University of Trieste) for several years and several renowned positions, including President of the Società Italiana di Mineralogia e Petrologia (SIMP) for the two-year period 2022-2023.

About his interests

During his career, his main interests have included crystal chemistry of minerals (pyroxene, olivine and spinel) from mafic and ultramafic rocks and applications to petrological and thermodynamic problems. In addition, he also worked on Order-Disorder Mechanisms in synthetic and natural spinels and their dependence on composition, temperature and time. Based on these studies, a geothermometer based on Mg-Al exchanges was also revised between the T and M sites of the spinels. The results of this

What does SIMP represent for the scientific community?

The Società Italiana di Mineralogia e Petrologia, established in Pavia in December 1940, serves as an inclusive platform for researchers and enthusiasts engaged in Mineralogical (*sensu lato*) studies. Moreover, it facilitates the liaison between Italian researchers and their international counterparts. Indeed, SIMP is affiliated with and constitutes an integral part of scientific societies, including European ones, wherein it co-publishes an important journal, the European Journal of Mineralogy (EJM). Additionally, it collaborates with the International Mineralogical Association (IMA), where numerous members hold Chairperson positions in sections, notably in mineral classification. It also collaborates with Italian scientific societies for the organization of conferences, schools, Distinguished Lectures, and, more broadly, for the promotion of Mineralogical disciplines and Geology. Consequently, it is a scientific society that aims to stimulate Mineralogical studies and provide opportunities for the scientific advancement of its members, particularly the younger cohort, through awards and contributions to facilitate participation in conferences and schools.

In your research career, what was the most enriching experience for you and the most memorable one?

My career as a researcher, which began in 1983, has encompassed numerous experiences, particularly in the field of crystal chemical and crystallographic studies on minerals found in mafic and ultramafic rocks, especially pyroxenes, olivines, and spinels. In addition to this, I have had experiences in the study of clay minerals and also in applied research on the determination of asbestos in artifacts. However, the most enriching experience, which has given me the most satisfaction and opportunities to forge scientific relationships with other scholars, was participating in a research project that originated in the 1980s and involved almost all Italian mineral-petrographic groups, namely the national project "Crystal chemistry and Petrogenesis." This project allowed us to delve deeper into the relationships between structure, chemistry, and genesis of minerals, and it provided new impetus to Italian mineralogical research and beyond, considering the international collaborations established by the various research groups.

research have been presented at national and international conferences and are the subject of over a hundred published contributions in national and international journals.

For his scientific activity, a new mineral (IMA2020-056) belonging to the supergroup of the tourmalines was dedicated to him in 2022, the "princivalleite", $\text{Na}(\text{Mn}_2\text{Al})\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})\text{O}$, found in a pegmatitic vein in the Veddasca Valley (Luino area, Varese, Lombardy, Italy).

When you were a student, what sparked your interest that led you to the achievements of your career in geosciences?

My interest in Earth Sciences started back in high school; I was drawn to the sciences, particularly the natural sciences. What convinced me to enroll in Geology was a lecture on the "history of the earth." Once enrolled in Geology at the University of Padova, my enthusiasm for Earth Sciences grew, especially thanks to the field trips that allowed us to experience geological phenomena first-hand. My interest in mineralogical studies developed during the last two years of university while taking some courses. Specifically, I was fascinated by the courses on crystallography, volcanology, and crystal chemistry. The professors of those courses made me appreciate the potential of those subjects and their possible applications in various scientific fields, not just in geology. They also sparked my curiosity and desire to deepen my knowledge. During the completion of my Thesis, I had the opportunity to visit other universities and access their laboratories for single crystal diffraction collections, which also allowed me to meet the professors there, particularly in Pavia and Perugia. Working alongside them was truly instructive and stimulating.

During your career, you have had many directorships and chairmanships of geological societies and Earth Sciences departments, would you be able to define what, if any, is a particularly common problem that recurs in today's geosciences and society?

Throughout my forty-year career, I've held various positions both at the University of Trieste and nationally. At the university, besides being the Director of the Department of Earth Sciences, I've been part of the Academic Senate and the Board of Directors. Nationally, I've served as the president of the National Group of Mineralogy and, most recently, of our SIMP Society. Apart from administrative experiences, where the biggest issue lies in excessive bureaucracy, which is common to all disciplines, whether scientific or humanities, I've also had experience as the coordinator of study programs, specifically in Environmental Science and Technology, always in connection with Geological Sciences studies. The course I had the honour to coordinate had its ups and downs in enrollments, especially when the *numerus clausus* was introduced, only to skyrocket in enrollment numbers once it was abolished. Geological Sciences, on the other hand, have seen a constant decline over the years regardless of any *numerus clausus*. For me, this is a fact that doesn't have entirely rational explanations, given that every institution offering geosciences puts in a lot of effort to bring geosciences into schools: guided tours, conferences, teacher training courses, as well as participating in PLS (*Piano Lauree Scientifiche*). Unfortunately, in high schools, geosciences are not taught in the last two years when students are about to choose their university path, and furthermore, the teaching of geosciences is not always done by graduates or experts in geosciences. This is a significant wound because, in



this way, there is no stimulus to delve into and become passionate about these subjects. Yet, it's enough to remember, for example, how important the figure of a geoscientist is in caring for and preserving the territory, and this is not only a problem for study courses but also for today's society. Another serious problem is dropouts, often caused by students switching to other degree programs where they haven't had access in the first year. The lack of "vocations" in geosciences has also been addressed globally, and the issues are similar in many countries. It's truly a shame, considering that geosciences allow us to study the territory we live in and often provide solutions for its safeguarding.

September 2018
At the Museum of Mineralogy and Petrography (Department of Mathematics, Informatics and Geosciences): inauguration of the new installation of a fossil araucaria tree from the petrified forest (Arizona, USA).

May 2017

During an educational excursion to the Magnetite mine, Capo Calamita, Elba Island.



What soft skills and competencies do you think we need to teach to young students and we need to develop in order to relate to society, so that our work/research is more convincing and appreciated? What skills and competencies are sought after in geoscientists today?

It's important to convey to young students the enthusiasm with which we tackle the various issues related to our research so that they, too, will be encouraged to delve deeper into what they are studying. This way, they can transmit to their peers, colleagues, and eventually to society the importance of geoscience studies. A serious research/work, if well communicated, will be more convincing and appreciated. Communication thus becomes crucial, and it wouldn't be wrong to include a scientific communication course, at least among the elective courses, in our study programs. I'm obviously talking about being able to communicate appropriately and understandably about the activities that a geoscientist is carrying out. Moreover, it's essential for geoscientists to be prepared to collaborate in teams, engaging with fellow professionals to tackle challenges comprehensively. This collaboration encompasses various disciplines within geosciences, exemplified by the fruitful exchanges among researchers from different universities facilitated not only by the sharing of equipment but, more significantly, by the exchange of knowledge.

Do you have any advice for young people who want to study geological sciences?

The advice I'd like to give to those who want to study geological sciences is to be curious and always delve into all aspects related to the geological phenomena they encounter. Observing our surroundings and considering methods of preservation are key. Additionally, it's important to learn and work collaboratively in groups, enhancing proficiency in a foreign language. This linguistic skill is beneficial not only for academic pursuits but also for those entering the field of Geology, especially if they anticipate working in industries or construction sites, where interaction with both labourers and other professionals is inevitable. Furthermore, I would recommend paying attention to the digitalization of information, as it plays an increasingly crucial role in the field. Being proficient in utilizing and analysing geological data using various software tools is essential for modern geologists, as it allows for more efficient and accurate analysis, interpretation, and communication of geological findings.

Patrizia Fumagalli



Patrizia Fumagalli is a full professor in Petrology at the University of Milano (Italy). She completed a degree in Earth sciences at the University of Milano in 1997 and a PhD in high-pressure experimental petrology in January 2000. After a postdoctoral fellowship at the University of Michigan (USA), she was introduced to first-principles calculations as a tool to unravel the high-pressure behaviour of phases.

About her interests

Her main interests lie in the understanding of deep geological processes such as metamorphic phase equilibria, crystal chemistry, thermodynamics and volatiles transfer in subduction zones and petrological implications for lithospheric evolution at extensional settings.

She combines various methodologies in different disciplines (e.g. mineralogy, geophysics, first-principles calculations) with the petrology of subduction zones to define the thermodynamics and crystal chemistry of high-pressure

What does SIMP represent for the scientific community?

When thinking about the Società Italiana di Mineralogia e Petrologia (SIMP), I genuinely believe it can be a cornerstone of the scientific community, especially for the new generations, the future of research and the dissemination of mineralogical, petrological, and geochemical sciences in our society; a cradle of relationships that sometimes, serendipitously, lead to the creation of unique professional careers. When I applied for the role of Vice President of the SIMP, I was primarily driven by a sense of belonging to a community, albeit a small one, that represents decades of scientific research and progress in the fields of mineralogy, petrology, and geochemistry in all their facets. Now more than ever, our disciplines must open to the outside world alongside all other geoscientists. For this reason, the SIMP also represents communication. The SIMP is community, it is opportunity, it is exchange.

Why did you choose science and, in particular, geosciences?

Curiously, there wasn't a particular interest that prompted me to choose geosciences. My academic career began with two fruitful years devoted to a mathematics degree. However, the choice of geosciences crept in as I attempted to apply mathematical structures to the exploration of natural phenomena. Being able to model deep processes, in conditions beyond direct human scrutiny, has always fascinated me. Thus, for example, I renewed the algebraic structures I encountered at an advanced level in the study of group theory in mineral systems. Or, for example, I found it easier to deal with the description and representation of multi-dimensional chemical systems (i.e. rocks), thanks to linear algebra.

Was there anyone in particular who influenced this choice?

The coincidence, the serendipity of finding myself in the basement study halls of the mathematics department alongside students enrolled in geology, propelled me into a new realm of science and sparked a desire to explore the fascinating world of geosciences, which is unfortunately still underrated within the realm of integrated sciences.

minerals (chlorite, phlogopite, amphibole, dense hydrous magnesium silicates).

She applies high-pressure techniques (diamond anvil cell, piston cylinder, multi-anvil module) and analytical techniques (X-ray diffraction, Raman spectroscopy, microanalytical geochemistry, scanning and transmission electron microscopy) to studies in the fields of materials science, ore geology and gemmology.

Today, she is the Vice President of the SIMP society.

Can you tell us about a memorable moment or experience in your career that made you particularly proud or excited?

The one moment that was truly memorable in my career was receiving the unexpected offer for a fellowship at the University of Michigan (Ann Arbor) from Professor Lars Stixrude. It was a turning point that catapulted me into an entirely new field: first-principles calculations applied to high-pressure crystal structures. That period was enlightening, as it showed me the breadth and diversity of methodologies in geosciences. I learned the importance of keeping an open mind and not limiting myself to a single perspective when it comes to scientific research. It still astonishes me when I think there are still researchers who divide disciplines based on the methodologies employed. The goal of our research is to understand natural phenomena, and embracing and exploring different paths only enriches our journey toward this common objective.

You are an experimental petrologist, what was the experience that enriched you the most?

Being able to create my own sample, my own rock, my own subject of study. Planning an experiment is pure creation, it requires imagination but also a knowledge of what is found in nature, an expression of profound processes in which we cannot directly participate. It's like miniaturising yourself and finding yourself inside the Earth. In Milano, we still prepare experiments starting from working at the lathe, producing small pieces of graphite and ceramics to assemblage the cell pressure. Then we go to the big presses, and there, we still need to have a foundation in electronics, physics, hydraulics, and, yes, a "problem-solving" attitude. But what enriches me greatly in conducting experiments is that often you don't find exactly what you expect, and thus new paths unfold, leading to further experiments and new challenges.

What does it mean to you to be a female scientist in geosciences? Can you share your experience as a female scientist in your career? Did you have any difficulties in reaching your goals?

Gender stereotypes are deeply ingrained cultural biases that permeate various aspects of society, including the realm of science. In scientific fields, women often face unique challenges due to societal expectations regarding family responsibilities and career



*An experiment is running:
what will we get out of
there?*



advancement. There is often a conflict between the rising period of scientific productivity and the time when women may choose to start a family. This can create obstacles for women in pursuing and maintaining successful careers in science. Addressing parental responsibilities is an area where there are no substitutes for a woman. I still recall the breaks between lectures to breastfeed my daughter, who waited (adequately supervised) in my office.

While progress has been made with the introduction of policies such as parental leave and career considerations for women in science, there is still work to be done. I believe that the true revolution must go far beyond simply applying quotas to “promote” the role of women. Personally, I would prefer to be recognised as a scientist first and foremost, rather than as a female scientist. I would prefer to be

assigned a role, for example in selection committees, because of my abilities and not simply to fulfil a quota for women decided a priori.

In my ideal world, gender neutrality and meritocracy would prevail in scientific fields. Individuals would be evaluated based on their skills, expertise, and contributions, rather than their gender. This environment fosters fairness, encourages diversity, and maximises the potential for innovation and advancement. It’s a vision worth striving for, as it promotes equal opportunities and empowers individuals to excel based on their merits alone.

Do you have any advice for young people who want to study geological sciences?

Be keen observers! Observation is the foundation of the questions humans ask to understand nature and the world around them. Be curious! Science arises from curiosity and the desire to understand why. Be creative! Imagination propels research towards knowledge. Foster relationships and exchanges of perspectives! Read, stay informed, and study! From dialogue and knowledge, a new path always emerges. Last, do not stop dreaming!

Alessandro Pavese
received the Plinius
Medal 2023

Alessandro Pavese



Alessandro Pavese is a full professor of Mineralogy at the University of Torino since September 2016. He has been Area President (Earth Sciences, University of Milano) and Director of the Earth Sciences Departments of University of Milano and University of Torino. He has been SIMP President, representative of Earth Sciences at the Italian Synchrotron Light Society, President of the Gemmological Foundation Scientific Committee (Milano), Associate Editor of the European Journal of Mineralogy, corresponding member of the Academy of Sciences of Torino, and vice-president of the European Mineralogical Union.

About his interests

He directed his research activity to both the “basic” and “applications” fields. As for his research, he dealt with the stability-instability phenomenology of mineral phases and exchange processes in non-environmental regimes (high pressure and/or temperature), with particular attention to the “triggers” transformation. As for industrial research, he was interested in the reactivity of systems complex, multiphase, at high temperatures or in a particular chemical environment. Such research was conducted both with the use of modelling

What does SIMP represent for the scientific community?

SIMP is the reference Association for scientists from both Accademia and Scientific Institutions and anyone else interested in the disciplines relating to Geomaterials at large. Geomaterials as seen in the natural environment for the comprehension of the large-scale planetary processes, and in environmental and anthropogenic contexts, for their exploitation.

In your research career, what was the experience that enriched you the most and of which you have a most beautiful memory that you carry with you?

It is challenging to choose the “best scientific moment”, as there have been so many, and quite different in nature from each other. In this view, I am selecting the one that most vividly impressed in my memory: the first time I entered the Rutherford Laboratory to perform a powder neutron diffraction experiment at the beamline POLARIS. It was 1990, and I reached ISIS from London, where I was collaborating with the computing group of Mineral Physics of the Geological Department at the UGC. The experimental room of ISIS, wherein the beamlines are gathered, gave me the sensation of the vast and collective effort coordinated around the research activity to delve into the microscopic world at the atomic scale – something I had never experienced before. I was used to laboratory facilities that represent the backbone for research; seeing a large-scale facility impressed me profoundly and was the boost toward embracing definitely the profession of my life.

What was the best moment of your career?

The PhD Course in Crystallography made me deeper and deeper involved in Mineralogy and avid to pursue the cutting-edge research I was dealing with. Therefore, when I learned that I had been selected for a position as a researcher in Mineralogy by the Earth Sciences Department of the University of Milano, I realized that my dream of entering professional research was becoming a reality. It was 1991.

techniques and with the use of laboratories conventional and "large-scale facilities". The research activities are documented by over 130 publications in international journals.

During your career, you have had many directorships and chairmanships of geological societies and Earth Science Departments, would you be able to define what is/are, if any, a particular common problem that recurs in the geosciences and today's society?

It is a really complex question, touching a paradoxical situation. Geosciences significantly impact most aspects relating to "global sustainability, climate change and so on" in terms of topics and methodologies. Nevertheless, we are suffering from a "vocational" crisis worldwide. I think this is the effect of the combination of different aspects. The starting point is the high interdisciplinarity of our themes, which have been "cannibalised" by other areas. In such a light, we should better assert our field of purview and the borders that specifically contour and locate the required competence. Besides this, we must improve our efficacy in communicating. Many youths do not know what we actually do, or misinterpret our job and are convinced we negatively impact on the environment, or are genuinely aware of only a speck of the activities pivoted by us.

In your research you have always been very interested in the relationships between theory and its applications, collaborating with many public and private laboratories, a connection that is not always trivial and immediate. What soft skills and competencies do you think we need to have to be able to talk to people not in our geological field, for our work/research to be convincing and valued? What skills and competencies are sought after in young people today?

I think it is important to underline the crucial connection between resources, which can always be tacked down to "Georesources", and our intrinsic competence, which involves both the "objects" (be they solid or fluid systems, any way of our planet), their transformations and the methodologies to investigate them. In particular, in my relationships with manufacturing industries, I benefitted much from the intrinsic "practice" of dealing with complexity, which develops as a natural consequence of the topics we historically and traditionally have as cultural core business.

I take the liberty of suggesting to youths that they use more courage in introducing themselves in contexts that appear to be disjointed from ours. Keep in mind that dealing with geological complexity helps one develop transversal knowledge and know-how that is crucial to treating a wide variety of questions.

Do you have any advice for young people who want to study geological sciences?

My suggestion is that they keep in mind that they are entering a field that offers an extraordinary variety of chances. The high degree of interdisciplinarity requires a deep and very solid education. In this light, they must convince themselves of the need to seriously invest much time to become professionals at large in Geology. I believe that those who tackle Geological studies intending to put in effort and enthusiasm will be well repaid with many satisfactions, whether they will be involved in research or in the profession.

Yves Moëlo has been nominated Honorary Fellow in 2022

Yves Moëlo



Yves Moëlo is well-known in the international mineralogical community for his contribution to mineral systematics and, in particular, for his seminal work on the crystal-chemistry and systematics of sulfosalts. In this context, he was the senior author of the report of the sulfosalt sub-committee of the IMA Commission on Ore Mineralogy.

About his interests

Since the beginning of his research, the scientific activity of Yves Moëlo has mainly focused on the role of minor chemical constituents in the stabilization of complex crystal structures. He also focused on ore mineralogy (along with ore mineralogists and geologists of the French geological survey) and on the solid-state chemistry of synthetic chalcogenides, collaborating with chemists-crystallographers and being involved in the study and description of new mineral species (~40 new species).
The relevant

What, in your opinion, does SIMP represent for the scientific community?

My contact with SIMP was gradual. First, in 1984, during an excursion by the French Society of Mineralogy and Crystallography in Tuscany (Apuane Alps and Elba Island - first contact with Paolo Orlandi). Then, the participation in the XVI general meeting of the IMA in Pisa (September 1994). Finally, the commitment to a close and very human scientific collaboration with Italian mineralogists at the end of the 1990s (Paolo Orlandi, Pisa, and Filippo Vurro, Bari, and associated researchers). This experience made me appreciate the dynamism of the SIMP: organization of conferences, field trips, and close contacts with amateurs. All this with the promotion of the mineralogical richness of Italy, in which I had the pleasure of participating.

Reflecting on your extensive collaborations in Orléans and Nantes, could you share a particularly memorable or impactful experience from your time working with ore mineralogists, geologists, and chemists-crystallographers in these research environments?

There was a strong development of mineral systematics due to the automatization of analytical methods, first during the 1970s for electron microprobe, and secondly during the 1990s for crystal structure resolution through X-ray single-crystal diffraction study. It was a great pleasure for me to contribute to this scientific evolution in the field of sulfosalt and sulfide mineralogy. It helps ore geologists and geochemists for a better knowledge of paragenetic successions, the partitioning of minor and trace elements between sulfides, and metallogenetic processes.

Given your significant contributions to the description of over 40 new mineral species and your role in coordinating the Sulfosalt committee, can you outline what have been the greatest challenges and satisfactions during your scientific career?

My first step (at Orléans), under the direction of Roland Pierrot and Z. Johan (Geological French Survey, Orléans), C. Lévy and B. Cervelle (CNRS, Paris University), was the acquisition of experience in ore microscopy and microprobe analysis, through sampling of numerous sulfosalts in various sulfide ores. It opened international collaborations (E.

contribution of Yves Moëlo to Mineralogy and, in general, to mineralogical crystallography is proven by his publication record (more than 120 papers in the most important international journals, with more than 2100 citations. H index = 24).

For these reasons, in 2022, Yves Moëlo has been nominated Honorary Fellow of the Società Italiana di Mineralogia and Petrologia.

Makovicky, Denmark; N. Mozgova, Russia; J. Jambor and D. Harris, Canada, etc.), a basis for the activity of the Sulfosalt committee. I also acquired experience in the synthesis of lead sulfosalts and chloro-sulfosalts with C. Maurel (CNRS, Orléans).

The second part of my career was performed at the Institut des Matériaux de Nantes (IMN, Nantes University - CNRS), specialized in solid-state chemistry (in the team of A. Meerschaut, under the direction of the Academician J. Rouxel). It permitted the development of the crystal-chemical study of synthetic compounds with layered non-commensurate structures related to natural chalcogenides (cylindrite group) on the one hand. On the other hand, the experience of crystallographers was applied to the crystal structure description of new species discovered by Paolo Orlandi, using the principles of modular analysis established during the 1980s by E. Makovicky.

How do you feel about having a mineral, moëloite $[Pb_6Sb_6S_{14}(S_3)]$, named in recognition of your scientific activity in the Apuan Alps?

Moëloite (defined in 2002) is the natural counterpart of a new compound synthesized during my thesis (1982). It was discovered by Paolo Orlandi (Pisa University) at the Ceragiola marble quarry (Apuan Alps). It perfectly symbolizes the scientific collaboration developed between the Pisa and Nantes Universities.

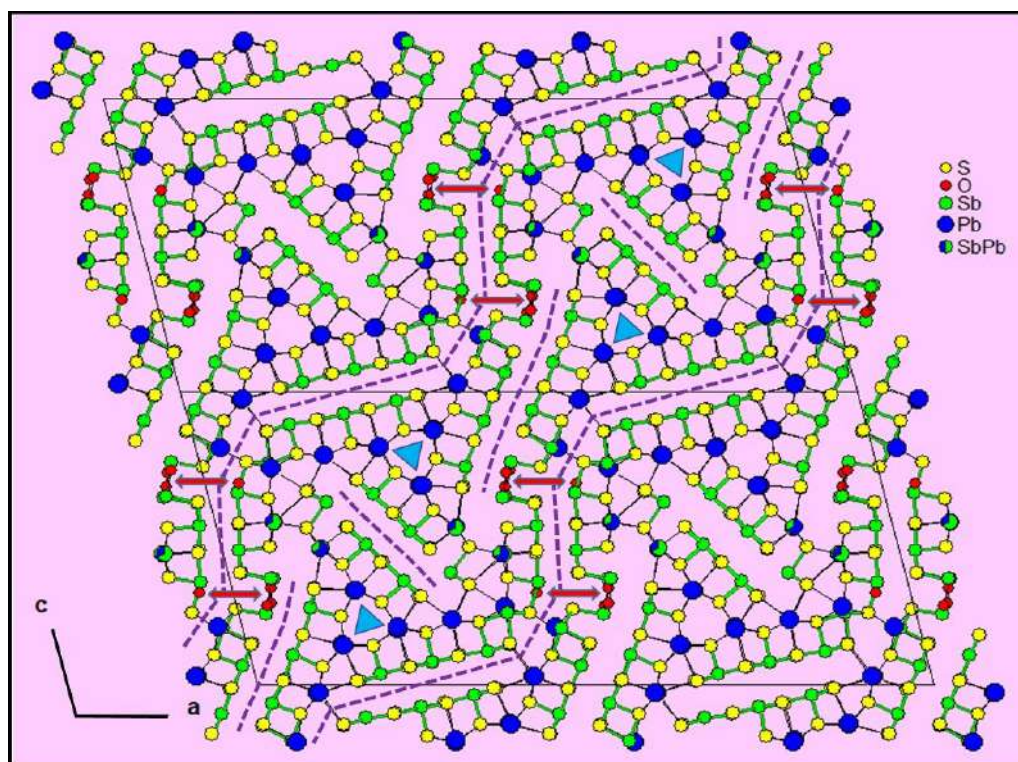
What was the experience that enriched you the most?

Since the end of the 1990s, the collaboration with Paolo Orlandi, together with Alain Meerschaut's team of solid-state chemists, about the crystal-chemical study of complex sulfosalts from Apuan alps (among which the first oxy-sulfosalts). This collaboration is still active today with Cristian Biagioni (Pisa University) and Luca Bindi (Firenze University).

What was the best moment of your career?

I prefer to indicate four significant moments in my mineralogical career:

- As an amateur, together with a friend during the 1970s holidays, the discovery of rare minerals (especially REE carbonates of the bastnäsite series) in the talc deposit of Trimounts (French Pyrenees);



Rod-layer organization of scainiite crystal structure (Moëlo et al., 2000).

- In 1979, the redefinition of dadsonite as a lead chloro-sulfosalt (only one Cl for 60 S atoms in the unit formula);
- In 1999, together with Paolo Orlandi and Alain Meerschaut, the definition of the first oxy-sulfosalt, scainiite, $Pb_{14}Sb_{30}S_{54}O_5$;
- Very recently (2023), the description of a trigonal variety of pyrite by the morphological study of centimeter-size crystals from the Madan Pb-Zn ore district (Bulgaria).

Do you have any advice for young people who want to study geological sciences (min-pet-geochemistry)?

Of course, everyone must master a specialty, anchored on the study of a certain type of geological object. Nevertheless, we must not forget that geosciences, by their objects, are historical sciences, where phenomena interact on the most diverse scales, from the atomic level to the vastest levels, planetary as well as astronomical. It is, therefore, very rewarding to link a result obtained at one scale to data specific to other scales. For instance, the detection of chlorine in dadsonite led to highlighting the contribution of Triassic formations as a source of chlorine. Ore parageneses containing dadsonite, in particular, may result from the *in situ* remobilization of Variscan stibnite deposits through late superimposition processes, observed from the Harz Massif (Germany) to Morocco.

In conclusion, throughout my career, I have had the pleasure of meeting numerous specialists, both French and foreign. They have brought me a lot, both through their scientific skills and their human value. I would particularly like to express here all my gratitude to Paolo Orlandi, whose high competence I appreciated in the field of mineral systematics.

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**PREMIO ANGELO
BIANCHI
2023**

Valentin Basch



Area of Expertise:
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What were the reasons that led you to choose geology as a career? And what does geology mean to you?

I was not exactly the typical rock-collecting child, although the Earth system always fascinated me; the raw force of nature that translates into earthquakes, volcanoes, and geysers definitely had a hook on my curiosity. What sealed the deal is that growing up, I was increasingly fond of being outdoors, in the wilderness, and natural sciences such as geology could offer the mountains as your scientific playground. My research is also my passion, and I think it is the best driver there is.

My scientific activity is focused on the petrology and geochemistry of the oceanic lithosphere. My research is primarily aimed at constraining the magmatic and exhumation processes occurring in oceanic environments, from: *i*) formation of melt during decompressional mantle melting, to *ii*) reactive melt transport in the upper mantle and lower gabbroic crust, *iii*) (reactive) crystallization of melts, and *iv*) mylonitic deformation and metasomatism during exhumation of Oceanic Core Complexes. The combination of field observations, micro- to nano-scale structural analyses and geochemical characterization of minerals and bulk rocks allows a detailed investigation of the complexity of magmatic processes occurring in oceanic environments. These studies are conducted in all the oceanic environments, from ocean-continent transition to slow- and fast-spreading ridges and back-arc basins.

My current research focuses on the efficiency of aggregation of oceanic melts during their upward migration in the upper mantle and lower gabbroic crust. To date, oceanic environments are envisioned as formed from a single melt composition, i.e., fully aggregated Mid-Ocean Ridge Basaltic (MORB) melt, in turn driving a homogenization of the isotopic composition of the oceanic crust. By performing state-of-the-art *in situ* sampling and isotopic analyses, we demonstrate that oceanic melts feeding spreading ridges preserve a strong heterogeneity, even at fast-spreading ridges (East Pacific Rise). This will drive a new paradigm on the composition of oceanic melts and has a strong influence on our understanding of the compositional heterogeneity of the upper mantle through global cycles of recycling of the oceanic crust at subduction zones.



I received the Angelo Bianchi SIMP award based on my scientific activity and publication records. These peer-reviewed articles focus on understanding the Earth system, oceanic spreading, and global tectonic cycles. In a time when many studies and scientists are turning towards increasingly applied geology to monitor and predict the interaction between the Earth and humans, it is truly an honour to be recognised for studies of "fundamental science".

**PREMIO MAZZI
(EX PANICHI)
2023**

Fabrizio Tursi



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What were the reasons that led you to choose geology as a career? And what does geology mean to you?

I have been intrigued by minerals since childhood, as I received several as gifts from my aunt. Later, my curiosity about the internal structure and dynamics of our planet grew, thanks to the great aura of mystery left to me by my high school science teacher (a very good biologist) about the Earth Sciences. This made me want to know more about geology, which I consider a commodity of first necessity for the cultural progress of our society.

The main goal of the project “ENTHALPY – the intERplay betweenN mineral deformaTION mechanisms And fLuid Pressure localizes deformation in the drY lower crust” is to understand whether deformation and seismicity at depth are triggered by the different rheologic behaviour of minerals or driven by locally increasing $\mu\text{H}_2\text{O}$, inducing mineral reactions and changes in the volume of solids. In addition, ENTHALPY aims to determine the heat required to stabilize the new mineral assemblage during the shearing event. To achieve these goals, field observations are combined with analysis of mineral deformation mechanisms and mineral composition variations, measuring of H_2O content in nominally anhydrous minerals (NAMS), mass balance calculation and thermodynamic modelling. This approach is being adopted on ductile shear zones from the Serre Massif of Calabria and the Dora Maira Massif from the Western Alps.

The correlation of mineral deformation mechanisms to (i) H_2O contents in NAMS formed during high-strain events and to (ii) changes in the rock reacting volume tie the role of stress on mineral equilibria and that of changes in internal extensive thermodynamic variables on strain localization. This information is crucial to understanding the seismic to aseismic creep evolution and localization of deformation in the deep Earth’s crust and subducting slabs. In particular, the adopted approach allows the investigation of the role of grain-scale pressure variations in driving mineral reactions and provides fruitful information on how changes occur in stressed systems and on the energetics of the system undergoing changes, highlighting how grain-scale instabilities impact on whole rock rheology.



The SIMP grant contributes to carrying out the necessary microanalysis on minerals, such as EPMA, FTIR, and EBSD, and provides financial support for travel costs.

**PREMIO MAZZI
(EX PANICHI)
2023**

Gianfranco Ulian



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What were the reasons that led you to choose geology as a career? And what does geology mean to you?

I pursued this career because I have always been inspired by the beauty and fascination for the order of natural solids, minerals, and crystalline solids, small (and sometimes rather big!) treasures with so many stories about the world and Universe we live in. I was also lucky to be guided on this path by people who helped me foster this passion day by day.

My research is focused on the characterization of the crystal-chemical and physical properties of minerals for various and manifold applications, e.g., in crystallography, biomineralogy, catalysis, sustainable materials and optoelectronics, using a multi-methodological approach. The goal is to understand how the crystal-chemical and physical properties originate, e.g., from the vicariance of elements or their vacancies, how to control them in synthetic analogues, and how to devise new applications for known minerals. Just as an example, one of the topics I am still pursuing is the role that minerals, in particular phyllosilicates, played when simple biomolecules (e.g., amino acids) organized into the complex macromolecules of life (e.g., proteins). Another research subject I am interested in is investigating the optical and electronic properties of bidimensional minerals, such as molybdenite and orpiment, for both basic knowledge and specific applications.

The originality of my research resides in the combined use of different experimental (XRD, SEM-EDS, scanning probe microscopy, vibrational spectroscopy) and theoretical approaches (static and dynamic ab initio simulations) to characterize minerals and crystalline materials and in the cross-correlation of their results, which allow obtaining quantitative data from the macroscale down to the atomic scale. This detailed knowledge is fundamental not only for mineralogy but also for the whole geoscience community, e.g., to understand important processes occurring on Earth, from its crust down to the mantle. My idea of research in mineralogy could be translated into "natural materials science", a way to understand better and valorise what our planet offers. Also, my research efforts aim to deepen our knowledge of the fundamental properties of different minerals, which in turn could reduce the anthropic footprint in the environment by devising novel applications for known phases.

It was a great honour for me to receive the "Fiorenzo Mazzi" SIMP grant, which represents a great recognition of my research. In addition to stimulating me to further investigate the properties of layered minerals, the award gave me international visibility, with the opportunity to attend an international conference, devise and find new collaborations, strengthen those in related fields, and acquire laboratory equipment.

**PREMIO TESI DI
DOTTORATO
2023**

Serena Dominijanni



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What were the reasons that led you to choose geology as a career? And what does geology mean to you?

I have always been passionate about science, and I think that Geology offers a playground involving knowledge from biology, chemistry, physics, and mathematics. I have chosen Geology as a career because I want to understand the natural world, how Earth can sustain life, and what we must do to manage its resources.

My research examines the physicochemical properties of composite materials, encompassing solid minerals, metal alloys, and glasses, up to deep telluric planetary conditions. During my PhD, I have explored the cycling of volatile elements through Earth's deep interior, simulating extreme conditions via high-pressure high-temperature experiments in the laboratory and at synchrotron X-ray facilities. Additionally, I conducted comprehensive analytical, thermodynamic, and spectroscopic measurements on the experimental products, both in situ and ex situ. Using a similar experimental protocol, during the last couple of years, I have been investigating the melting and physical properties of terrestrial planets, such as Mercury and Mars, and how they constrain their composition. Currently, I am focusing on the role played by the physicochemical processes in controlling the structure of melts to address the dynamics and the style of volcanic eruptions.

Among the various projects I worked on during these years, I would like to underline as one of the major findings the calibration of a thermodynamic model at high pressure to precisely monitor the oxygen fugacity during high-pressure high-temperature experiments. The novelty of this approach is related to its application for the first time to the diamond anvil cell (DAC), representing a first step in considering the DAC as a petrological tool to investigate mantle redox state at the extreme conditions of Earth's interior and provides a new method to calculate oxygen fugacity at high pressure.



I am honoured to have received the best PhD thesis award in the field of petrology. This recognition is an important achievement for my academic career and may open the doors to new job opportunities.

**PREMIO TESI DI
DOTTORATO
2023**

Maura Fugazzotto



Area of Expertise:

Georesources to mineralogy and petrology for environment and cultural heritage

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What were the reasons that led you to choose geology as a career? And what does geology mean to you?

Actually, I am not a geologist, but I feel adopted by the community of geologists. I am a Conservation Scientist, specialized in mineralogy and petrology applied to cultural heritage. Since my first experiences, I have worked with geological materials, and it was then that geology became my second home. For me, geology represents a perfect match between the importance of culture and the fascination of rocks.

My research was entitled "Functionalized geopolymers for restoration, new materials for brick masonries recovery in Mediterranean archaeological sites". With the aim of restoring ceramic materials, waste ceramic tiles and bricks were re-used as precursors for geopolymer mortars and prefabricated elements, thus providing alternatives to environmentally costly cement and traditional ceramics. The synthesis was carried out at room temperature in order to promote the sustainability of the tested products. The new materials were studied at a multi-scale level, both in terms of the gel formed (spectroscopic techniques and electron microscopy) and the physical and mechanical performance (compression tests, porosimetry, absorption, etc.). Finally, the efficiency when applied to the original substrates was studied, with particular emphasis on the interaction at the new/old material interface and the colour appearance.

I think that my research brings to the geoscience community a significant contribution, as the experimentation of geopolymers, which means eco-friendly alternatives to traditional materials, by recycling ceramic waste and their use in the field of cultural heritage conservation has been until now little explored. Today, in a world that is trying to face dramatic climatic conditions, researching new methods to build, restore, and create becomes essential. At the same time, the conservation field is suffering from the excessive and not rational use of cement, which is responsible for huge CO₂ emissions and does not show high efficiency in the restoration of ceramics and other materials. Furthermore, the enormous volume of ceramic waste represents a problem both for the environment and for the industries producing it. My research offers these problems a unique and valuable potential solution.

I consider the SIMP awards a precious opportunity for young researchers, who can be spurred to continue the open questions of their PhD thesis and present their results at conferences where they can meet interested colleagues and build connections. In my case, thanks to the SIMP grant, I will present the progress of my research at the international InART2024 Conference, which will take place in Oslo (Norway) in June.

**PREMIO TESI DI
DOTTORATO
2023**

Erwin Schettino



Area of Expertise:
Petrology, Mineralogy,
Geochemistry, Economic Geology

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What were the reasons that led you to choose geology as a career? And what does geology mean to you?

Geology is a hobby for me, and this is the reason that led me to choose it as a career.

My current research aims to track the melt evolution in the asthenosphere from the redox melting front to the surface. The main goal is to find the geochemical proxies that fingerprint the incipient stages of mantle melting in magmas erupted at the surface, as well as to elucidate the geochemical expression of the redox transformation that encompasses the melt ascent through the adiabat during mantle upwelling. To achieve this goal, I will conduct high-pressure/high-temperature experiments with a multi-anvil apparatus, and compare these results with the compositions of natural basalts erupted in different intraplate oceanic settings (e.g., Cape Verde, Iceland).

My research will contribute to assessing how melting begins in the deep mantle, as well as to understanding how a solid-state upwelling plume converts into a partially molten system delivering segregable and buoyant melts towards the Earth's surface.

The SIMP award will help my research by funding my participation in an international conference, where I can present my results and possibly discuss my project with several international experts in this field.



**BORSE DI STUDIO
PER L'ESTERO
2023**

Micol Bussolesi



Area of Expertise:
Ore Geology

Current position:
Post-Doc Researcher

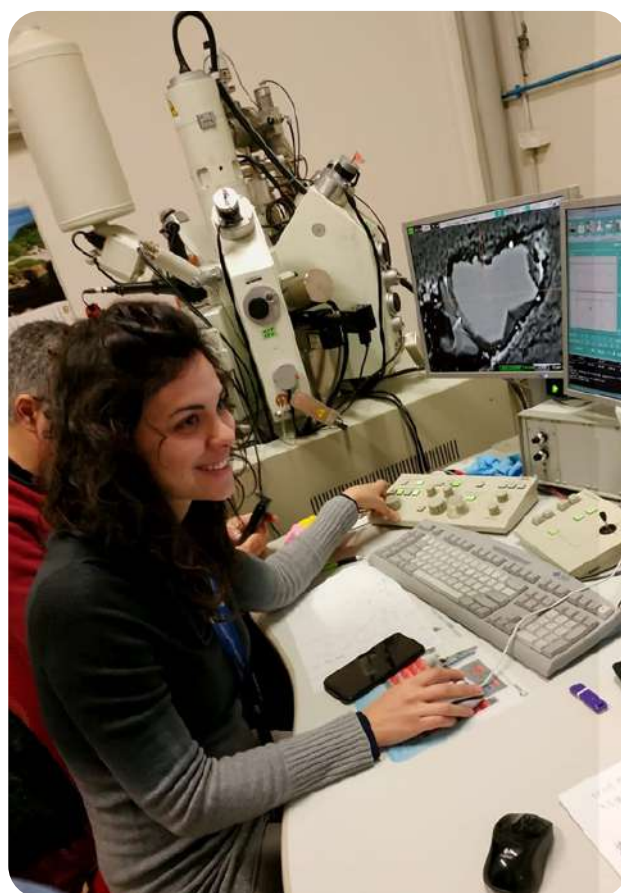
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What were the reasons that led you to choose geology as a career? And what does geology mean to you?

I chose a career in geology, especially an academic career, because I always liked the combination of fieldwork and analytical work, which allowed me to develop both practical and analytical skills. To me, geology is chasing interesting rocks around the world and trying to understand what they can tell us.

Platinum Group Elements (PGE) enrichments within ophiolites are strictly related to podiform chromite ore deposits. PGE are hosted within Platinum Group Minerals (PGM) and are sometimes enriched within sulfides. PGE-hosting mineralogical phases can be both primary (crystallized from the magma) or secondary (transformed during alteration events). This project proposal aims to apply a variety of chemical and physical techniques to fully characterize texture, morphology and mineral chemistry (comprising major, minor and trace elements) of PGE minerals, with the final goal of better understanding the genesis and later remobilization of these phases.

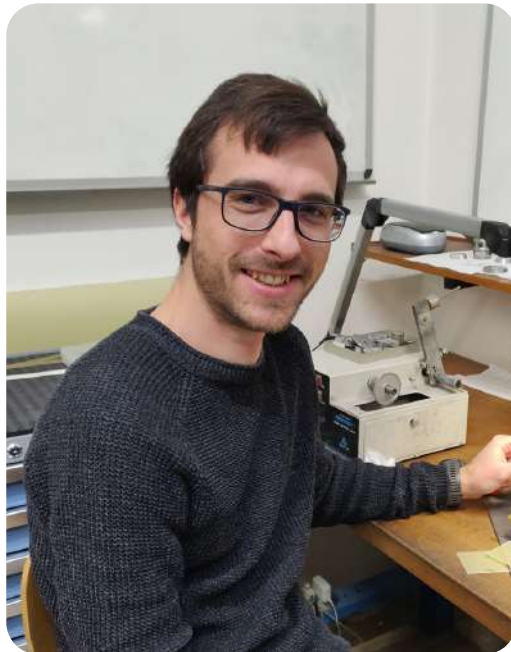


The research will focus on investigating Platinum Group Elements, which the EU considers Critical Raw Materials. PGE enrichment mechanisms in the ophiolite mantle and supra-Moho ultramafic cumulates are still largely understudied, but they can provide new insights into PGE behaviour in the upper mantle and new knowledge to economically target these mineralizations.

The award will allow me to do part of my research at the University of Western Australia. There, I will be able to work with experts in Platinum Group Elements geochemistry and ultramafic rocks petrologists and use UWA facilities to perform physical, mineralogical, and geochemical analyses on PGE-rich samples.

**BORSE DI STUDIO
PER L'ESTERO
2023**

Luca Toffolo



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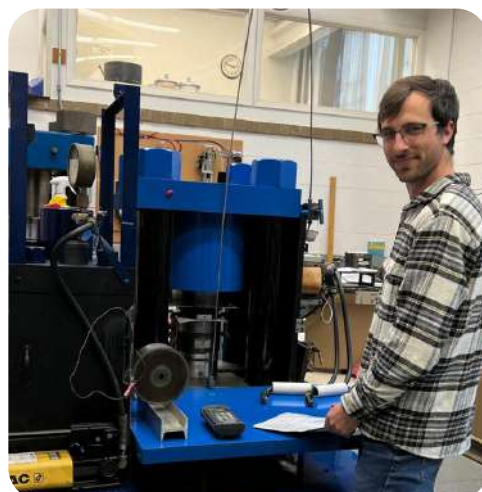
What were the reasons that led you to choose geology as a career? And what does geology mean to you?

I suppose studying geology stemmed from a desire to answer questions like "How did this form?" that arose whenever

I encountered minerals, rocks, fossils, and mountains. Geology, to me, is a key to deciphering nature. It offers a holistic perspective on Earth and its processes, revealing a deeper layer of wonder that transcends the immediate beauty of natural objects.

My research focuses on the behavior of volatile elements as they descend into the upper mantle through subduction zones. Currently, I am investigating the processes that govern the storage and release of molecular hydrogen within the subducted hydrous lithosphere. Specifically, I am assessing the solubility of H_2 in crystalline silica polymorphs and forsterite through high-pressure, high-temperature redox-buffered experiments conducted using both piston cylinder and multi-anvil apparatuses. The solubility of hydrogen is indirectly determined by analyzing the quenched experimental fluids with a mass spectrometer and comparing the results with thermodynamic models. Furthermore, residual hydrogen speciation and concentration are being evaluated using solid-state nuclear magnetic resonance spectroscopy, as well as both Raman and infrared spectroscopy.

The fast diffusion of molecular hydrogen poses a significant challenge for observations in natural samples and conducting analyses, thereby obscuring our understanding of the deep cycle of H_2 . Since H_2 acts as an electron donor, its mobility could potentially have a significant influence on the equilibria among minerals, fluids, and melts. Therefore, by investigating how the solubility of H_2 in silicates changes with variations in pressure, temperature, and redox state, we can gain insights into the processes that influence the redox conditions within rocks in the subduction channel and, ultimately, within the mantle wedge. In particular, the geological processes that can cause a release of H_2 stored in silicates

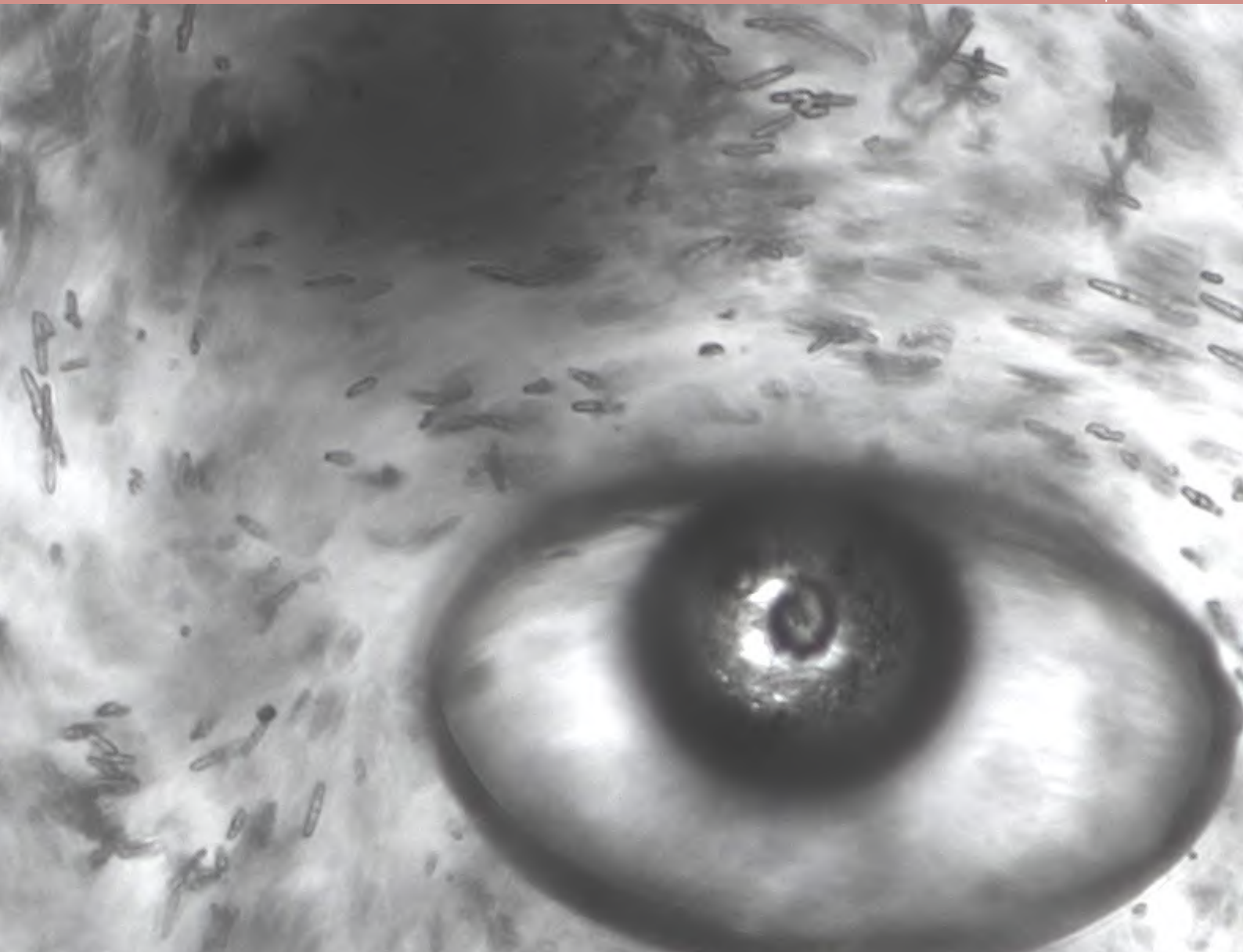


can generate highly reducing fluids, which may be involved, for instance, in the formation of some natural diamonds.

The SIMP scholarship afforded me the opportunity to engage fully in the scientific community at the Earth and Planets Laboratory of the Carnegie Institution for Science in Washington, DC, USA, the birthplace of modern experimental petrology. During my time there, I had access to state-of-the-art experimental and analytical facilities, including solid-state nuclear magnetic resonance spectroscopy.

Ph.D. Thesis Extended Abstracts

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High-pressure behaviour and crystal-fluid interaction of the ABC-6 zeolites: the case of erionite, offretite and bellbergite

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INTRODUCTION

Zeolites are a large group of hydrated aluminosilicates, widely spread in the first kilometres of the Earth's crust. They are characterized by an open aluminosilicate framework formed by the interconnection of channel and cage systems with "free-diameters" lower than 20 Å. Polar molecules (i.e., mainly H₂O) and alkali/alkaline-earth cations are hosted within the structural nanocavities, composing the extraframework population. The peculiar crystal structure of zeolites provides them with unique properties, among them: *i*) molecular sieving, *ii*) reversible hydration, *iii*) cation exchange, and *iv*) catalytic activity for the fractioning of hydrocarbon chains (Ghobar-kar et al., 1999; Li et al., 2021). The *International Zeolite Association* (IZA) recognizes the existence of more than 250 compounds with zeolitic structures, among those more than 80 found as natural species, highlighting the considerable crystallographic diversity and the scientific and industrial interest in zeolites.

In the last decades, the scientific community has shown a rising interest in the high-pressure behaviour (ranging from a few kbar to GPa) of zeolites, both natural and synthetic, in particular about the crystal-fluid interactions enhanced by pressure (e.g., Gatta & Lee, 2014; Gatta et al., 2018; Gigli et al., 2019; Comboni et al., 2020; Arletti et al., 2011). Given the zeolite's capacity to host and exchange H₂O, other small molecules or monoatomic species (e.g., noble gases), *in situ* experiments involving hydrostatically compressed zeolites, in potentially-penetrating mixtures of molecules, can provide a description of the *P*-induced crystal-fluid interaction phenomena in zeolites.

This Ph.D. project aimed at the investigation of the *P*-mediated crystal-fluid interaction in erionite (ERI framework type), offretite (OFF framework type) and bellbergite (EAB framework type), three members of the "ABC-6 group" of zeolites. The investigations were also performed on the synthetic counterpart of bellbergite, a polycrystalline sample with an EAB framework. The

purpose of this project is twofold, including both geological and industrial implications. From a geological perspective, studying the high-pressure behaviours of minerals, and the interactions between fluids and zeolites, represent a crucial initial step to better understand complex geological processes. Zeolites, found as alteration species in marine basalts or sediments, exhibit markedly higher H₂O content compared to commonly widespread hydrous minerals of the Earth's crust (i.e., amphiboles, micas, chlorites, ...) (Kastner, 1979). Considering the ability of zeolites to over-hydrate and dehydrate in response to *P-T* variation, it is reasonable to suppose that they act as fluid carriers during the early stage of subduction. In this light, a comprehensive description of the *P*-mediated over-hydration of commonly found natural erionite, along with the structurally similar offretite and bellbergite, was performed. On the other hand, from an industrial perspective, studies on the interaction between zeolites and various alcohol molecules represent a necessary step to open a new route in, for example, methanol chemistry. Under this light, applying a pressure gradient could serve as an effective route to enhance zeolites' adsorption capacity and then promote interaction and transformation of the sorbates. The experiments performed on synthetic EAB allowed direct observations of the different high-pressure behaviour and *P*-mediated crystal fluid interaction among isotopic materials: synthetic and natural zeolite. Additionally, the two investigated isotopic samples (i.e., natural and synthetic) were characterized by a different Si/Al ratio, unveiling the effect of crystal chemistry on the material behaviour. Furthermore, no crystallographic data at high-pressure were available so far for erionite, offretite and bellbergite, along with their elastic parameters. This study aims even to shed new light on the pressure-induced deformation mechanisms, at the atomic scale, of three representative species of the ABC-6 group.

MATERIALS AND METHODS

Zeolites belonging to the ABC-6 group include hexa-

Table 1 Chemical formulae by EMPA-WDS analysis of the investigated samples. For the synthetic Na- and K-EAB, the charge imbalance is likely compensated by silanols and H^+ .

Sample	Chemical Formula
Erionite	$(K_{2.39}Ca_{1.99}Mg_{1.02})[Al_{9.02}Si_{27.05}]O_{72} \cdot 26.84H_2O$
Offretite	$(K_{0.93}Ca_{1.12}Mg_{0.67})[Al_{4.77}Si_{13.26}]O_{36} \cdot 10.50H_2O$
Bellbergite	$(Na_{0.76}K_{1.73}Sr_{2.28}Ca_{4.93})[Al_{17.46}Si_{18.63}]O_{72} \cdot 28.03H_2O$
Na-EAB	$(Na_{9.9})[Al_{12.4}Si_{23.6}]O_{72} \cdot 17.3H_2O$
K-EAB	$(K_{11.2})[Al_{12.4}Si_{23.6}]O_{72} \cdot 16.4H_2O$

gonal structures that can be generated by the overlap of six-membered rings among three different positions (namely A, B, or C) by pure translation along the a and b axes. The rings are superposed along the c-axis direction with a characteristic stacking sequence in the A, B, and C positions, which is diagnostic of the framework.

The crystal structure of erionite (ERI framework type, stacking sequence AABAAC) is characterized by the presence of three different types of cages superposed along the c-axis (Fig. 1). Similarly, in bellbergite (EAB framework, stacking sequence ABBACC) three different cages with a shorter length along the c-axis direction with respect to those of ERI framework occur (Fig. 1). Conversely, in offretite (OFF framework type, AAB stacking sequence) the absence of a six-membered ring in C position lead to the presence of a large 12-membered ring channel, absent in ERI and EAB framework (Fig. 1).

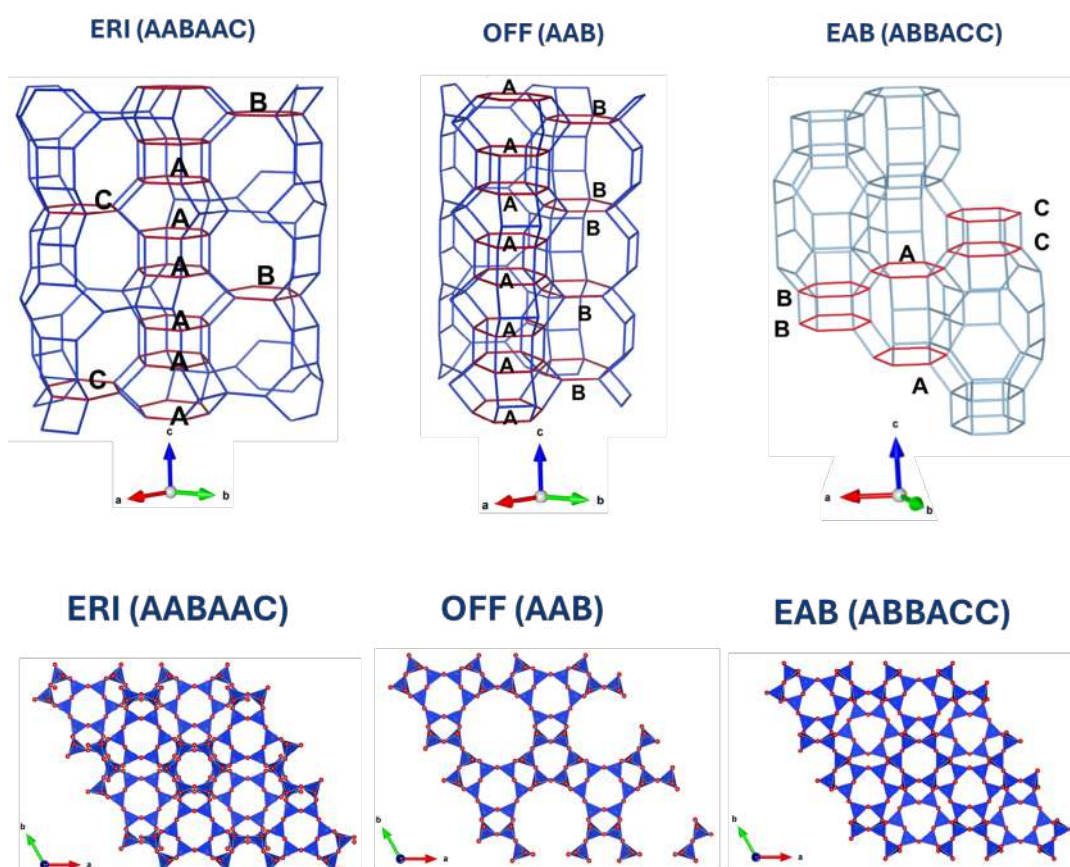
The three natural crystal samples and the two synthetic powders with EAB framework were chemically characterized by electron microprobe analysis in wavelength dispersive mode (EMPA-WDS). The chemical formulas are reported in Table 1.

The structure of the samples has been characterized with X-ray diffraction, to build a reliable structural model based on data collected at ambient conditions.

Experiments at non-ambient conditions

In situ high-pressure single crystal X-ray diffraction experiments were conducted at the ID15b beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) and the P02.2 beamline at PETRA-III, Deutsches Elektronen-Synchrotron (DESY) in Hamburg (Germany). The beamlines setup is described in Poreba et al. (2022) and Liermann et al. (2015). The non-ambient conditions were reached using a Diamond-Anvil-Cell (DAC) to generate hydrostatic pressure on the samples. The experimental protocol involved using different pressure-transmitting fluids to assess the intrinsic compressibility of the species and to stimulate the pressure-induced crystal-fluid interaction. In detail:

1. Experiments using 'non-penetrating' *P*-transmitting fluids, such as *daphne oil* (hereafter *d.o.*) or *silicone oil* (hereafter *s.o.*), aimed at determining the compressibility path and the elastic parameters of the minerals, without any interference of the *P*-transmitting fluid, setting a benchmark for the second-step.



- Experiments using ‘potentially-penetrating’ P -transmitting fluids, such as alcohols-water mixtures (i.e., distilled H_2O , methanol:ethanol: $H_2O = 16:3:1$ hereafter *m.e.w.*, ethanol: $H_2O = 1:1$ hereafter *e.w.*, methanol) or noble gases (i.e., Ne in its liquid state), to promote the P -mediated crystal-fluid interaction.

The experimental P - V data were modelled with an isothermal Birch-Murnaghan equation of state, using the EoSFit 7.0 GUI software, to calculate the bulk modulus $K_{V_0} = -V_0(\delta P/\delta V) = \beta_{V_0}^{-1}$, where β_{V_0} is the volume compressibility at room conditions (Angel et al., 2014).

RESULTS

Erionite

The compressional data obtained from the experiment using the non-penetrating silicone oil provide insights into the intrinsic elastic behaviour of natural erionite. The refined bulk modulus, calculated with a II order Birch-Murnaghan equation of state (Angel et al., 2014), resulted to be $K_{V_0} = 47(2)$ GPa. Interestingly, an increase in compressibility was observed in the *silicone oil* experiment above ~ 0.5 GPa due to the saturation of a peculiar deformation mechanism of the erionite cage (detailed discussion in Battiston et al., 2022).

The P - V analysis of the unit-cell evolution between the experiments using non- and potentially-penetrating PTFs suggested the occurrence of P -induced intrusion of H_2O . Therefore, the over-hydration of the structural cavities leads to a sort of ‘‘pillar’’ effect, resulting in lower bulk compressibility with respect to the pristine sample (Gatta & Lee, 2014; Gatta et al., 2018). The intrusion likely involves the erionite cage, showing the first evidence at relatively low pressure ($P \sim 0.2$ GPa), with an increase in

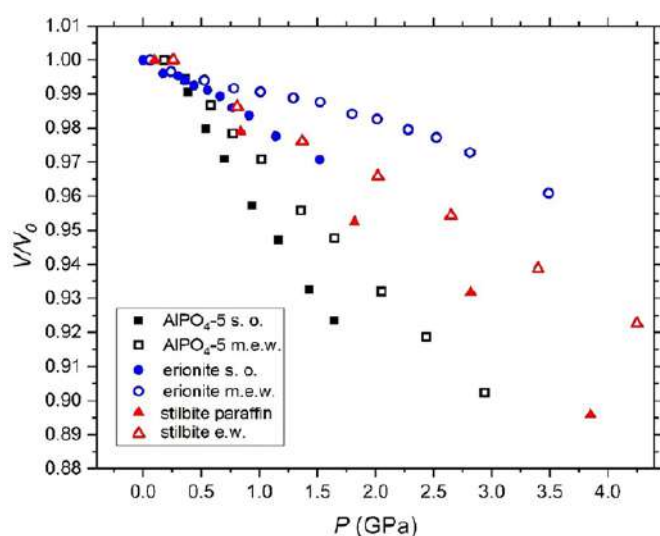


Figure 2 P -induced evolution of the normalized unit-cell volumes of the natural erionite of this study vs. synthetic $AlPO_4-5$ (Lotti et al., 2016) and natural stilbite (Seryiotkin et al., 2021), compressed in non-penetrating (full symbols) and potentially-penetrating (empty symbols) pressure-transmitting fluids.

magnitude at higher pressure.

A comparison with reported crystal-fluid interactions in other natural and synthetic zeolites reveals that the magnitude of the intrusion phenomena observed in erionite is surprisingly high for a natural zeolite with stuffed cavities (Fig. 2).

Offretite

The P - V data obtained using the non-penetrating *daphne oil* reflect the intrinsic compressibility of this zeolite. Interestingly, offretite exhibited a change of the compressional behaviour at ca. 1.83 GPa, without any pressure-induced phase transition. This change was marked by a significant decrease in bulk compressibility, being the refined bulk modulus, calculated with a II order Birch-Murnaghan equation of state (Angel et al., 2014), equal to $K_{V_0} = 59(2)$ GPa at pressures below 1.83 GPa, and $K_{V_0} = 28(2)$ GPa at pressures above 1.83 GPa. This variation is ascribable to a rearrangement of the extraframework configuration involving the migration of H_2O molecules, which enhances bulk compressibility (details in Battiston et al. 2023).

Experiments with potentially penetrating PTFs demonstrated the P -induced adsorption of new molecules within the large 12-membered ring (12 mRs) channels of offretite, resulting in an overall decrease of its bulk compressibility (Fig. 3). Comparing these findings on natural offretite with those of the structurally similar erionite, we observed that erionite is more efficient in P -induced adsorption of H_2O molecules, despite lacking a continuous large channel along the c -axis direction.

Neon (Ne) atoms can access the 12 mRs channels of offretite under the applied pressure, occupying the same atomic sites as the newly adsorbed H_2O molecules in experiments with potentially penetrating aqueous mixtu-

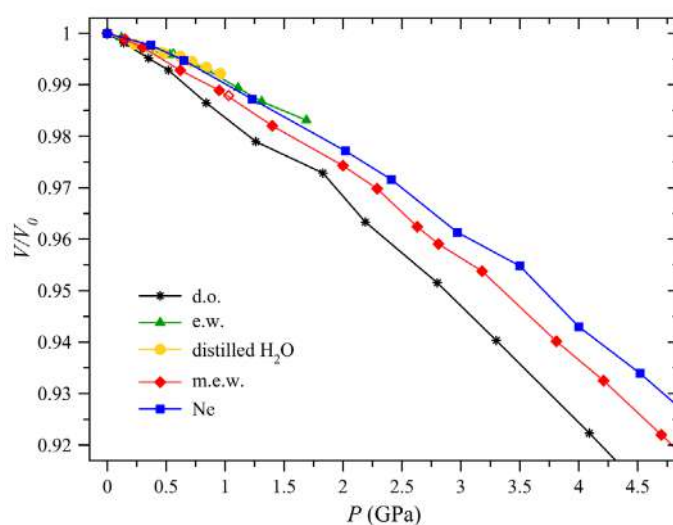


Figure 3 P -induced evolution of the normalized unit-cell volumes of the natural offretite of this study vs. synthetic $AlPO_4-5$ (Lotti et al., 2016) and natural stilbite (Seryiotkin et al., 2021), compressed in non-penetrating (d.o.) and potentially-penetrating (e.w., distilled H_2O , m.e.w. and Ne) pressure-transmitting fluids.

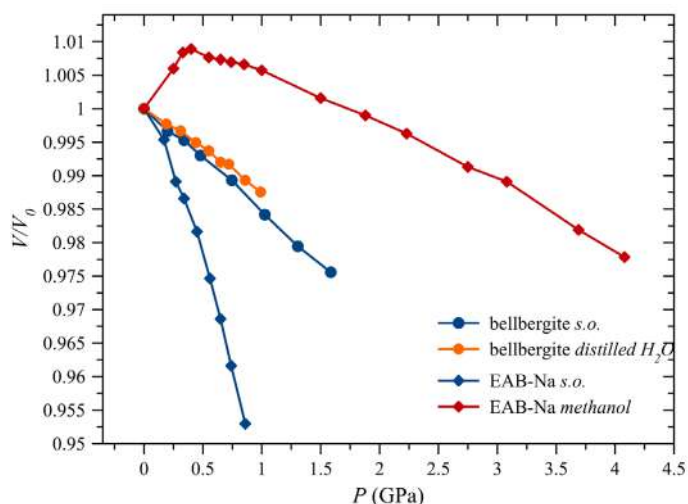


Figure 4 P-induced evolution of the normalized unit-cell volumes of the natural bellbergite and synthetic Na-EAB zeolite, compressed in non-penetrating (s.o.) and potentially-penetrating (distilled H₂O and m.e.w.) pressure-transmitting fluids.

res. These findings open a new route about the Ne cycle in nature, highlighting the potential of open-framework silicates to trap Ne under the combined pressure and temperature conditions, making zeolites potential carriers of Ne at shallow depths.

Bellbergite and synthetic analogues

In a non-penetrating fluid, the refined isothermal bulk modulus of natural bellbergite, calculated with an II order Birch-Murnaghan equation of state (Angel et al., 2014), resulted to be $K_{V0} = 62(1)$ GPa, while the synthetic samples showed markedly higher intrinsic compressibility, being their bulk moduli equal to 16(4) and 19(5) for K and Na end-member, respectively. The different compressional behaviour reflects the different nature of cationic and molecular extraframework populations among the samples (Battiston et al., 2024).

This is also evident from experimental data with potentially penetrating fluids, where the magnitude of crystal-fluid interaction is significantly higher in synthetic EAB, while it is modest in natural bellbergite and seems to occur only under compression in distilled H₂O (Fig. 4). Furthermore, both synthetic EAB samples show a remarkable unit-cell volume increase within the first 0.4 GPa when compressed in methanol, indicating a significant interaction with this molecule. In contrast, methanol does not significantly penetrate natural bellbergite.

DISCUSSION

The key role of the extraframework population on the bulk compressibility of a microporous structure with channels or cavities has already been widely described (e.g., Gatta & Lee, 2014; Gatta et al., 2018; Arletti et al., 2010). The experiments here performed made it possible to calculate the intrinsic compressibilities of the three

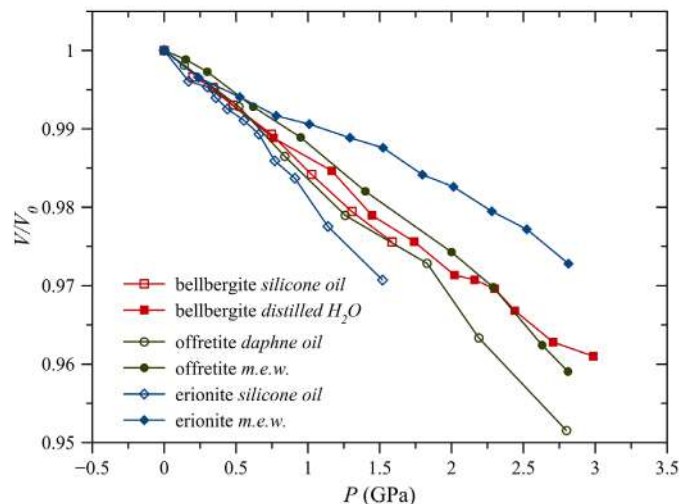


Figure 5 Comparative P-induced evolution of the normalized unit-cell volumes of the three natural zeolites here investigated, compressed in non-penetrating (s.o.) and potentially-penetrating (distilled H₂O and m.e.w.) pressure-transmitting fluids.

zeolites never investigated so far, revealing that erionite has the highest compressibility, followed by offretite and then bellbergite. The lower compressibility of bellbergite is likely a consequence of the high aluminium content in the framework, which requires a large number of extraframework cations within the structural cavities to balance the negative charge of the framework. Conversely, the higher compressibility of erionite, if compared to the structurally similar offretite, is ascribable to the higher structural flexibility of the framework (Battiston et al., 2023), governed by tilting of the tetrahedra, which act as rigid units around the O-hinges (Gatta, 2008), even in the first kilobar.

Regarding the crystal-fluid interactions, the experimental data reveal a higher pressure-induced adsorption capacity for natural erionite, followed by offretite and then bellbergite (Fig. 5).

Comparing the results of zeolites with EAB frameworks, the higher pressure-induced adsorption capacities of synthetic zeolites can be ascribed to some factors, including: *i*) a higher surface/volume ratio in synthetic zeolites, if compared to natural samples (i.e., powder vs. single-crystal); *ii*) a lower Si/Al ratio in the natural sample, resulting in a lower occupiable volume available for the new guest sites (Battiston et al., 2024).

The higher pressure-induced adsorption capacity of erionite compared to offretite, despite a lower occupiable volume within the unit-cell (11% vs 17%), is attributed to the different geometry of their frameworks. In offretite, the large 12-ring channels are not connected to each other on the (001) plane and are only accessible along the direction of the crystallographic *c*-axis. In contrast, the cages in erionite, although having a smaller occupiable volume than the channels, are interconnected, allowing higher accessibility and pervasiveness for the adsorption process (Battiston et al., 2022; 2023).

IMPLICATIONS

The crystal-fluid interaction experiments on natural zeolites revealed that all three species investigated here can increase and decrease their H₂O content in response to pressure. Notably, natural erionite exhibited the highest magnitude of over-hydration ever observed in a natural zeolite when compressed in an aqueous medium. This finding is significant, given erionite's widespread occurrence in various natural environments, including oceanic basalts as an alteration product (Hay & Sheppard, 2001; Kastner, 1979). Although less common than other hydrous minerals like amphiboles and micas, zeolites contain a higher H₂O content (even up to 20 wt.% at ambient conditions). Overhydration occurs at moderate pressure (~0.5 GPa) and ambient temperature, within the zeolite stability range, indicating that geological fluids can interact with these zeolites, enabling them to act as water (or other small molecules) carriers. Zeolite-rich basalts, subducted under moderate pressure and temperature conditions, can efficiently absorb and subsequently release molecules and cations. Therefore, the role of zeolites in fluid transportation within geological systems should be carefully reconsidered.

The remarkable methanol adsorption observed in synthetic EAB is particularly promising for methanol chemistry. This suggests that EAB-type zeolites could be suitable for MTH (i.e., *Methanol-To-Hydrocarbons*) processes, enabling the production of hydrocarbon products without the use of fossil oils as raw precursors. Considering the findings of this study, a dealuminated EAB sample with an increased Si/Al ratio could be a promising candidate for future research into pressure-mediated zeolite-methanol interactions.

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Gypsum Twin Laws and habits

An unexplored tool as a proxy for the chemistry of the original brine

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Depending on the depositional environment, gypsum exhibits different idiomorphic single and twinned crystal habits. In soils (Jafarzadeh & Burnham, 1992), desert regions (Shahid & Abdelfattah, 2009) and salt lakes (Warren, 1982; Mees et al., 2012), acicular, tabular-prismatic, lenticular, and twinned crystals are observed. In marine evaporites, mostly twinned and tabular gypsum crystals are found (Ortí, 2010). In caves and in Badenian evaporitic gypsum deposits, distinctive curved crystal structures (the so-called ram's horn and sabre gypsum) are observed (Wenrich & Sutphin, 1994; Panczner, 2013; Babel et al., 2015), whereas the most spectacular habits are related to the prismatic meter-sized single crystals and twins of Naica Mine (Mexico) (García-Ruiz et al., 2007) and in the Geode of Pulpì (Almería, Spain) (Canals et al., 2019), which grew by an anhydrite-gypsum thermally driven transformation by a self-feeding mechanism at low supersaturation values (Fig. 1).

These different gypsum habits were believed to reflect peculiar growth conditions (Lacroix, 1897). A better understanding of the environmental factors responsible for different gypsum crystal habits could have crucial implications for interpreting the origin of gypsum deposits formed in the geological past (Van Driessche et al., 2019). Consequently, many crystal growth laboratory experiments have been performed to establish which conditions favour specific gypsum habits. The acicular habit developed along [001] is the most common and representative of gypsum habit in a pure system (Craker & Schiller, 1962; Rinaudo et al., 1985), whereas tabular-prismatic and lenticular habits are promoted by different chemical composition of the mother solution (Cody, 1979; Rabizadeh et al., 2017; Reiss et al., 2019). Overall, saline waters with Na^+ , K^+ , Mg^{2+} , Sr^{2+} , Cl^- , and Br^- ions in solution reduce the [001] elongation of gypsum single crystals switching from acicular to tabular habit (Reiss et al., 2019), and organic molecules from green plants' decomposition promote the lenticular habit (Cody, 1979). Remarkably, twinned gypsum crystals have

often been observed both in natural environments (Warren, 1982; Shahid & Abdelfattah, 2009; Ortí, 2010) and by crystal growth laboratory experiments (Simon, 1968; Cody & Cody, 1989). However, twinned crystals have often been defined as "swallowtail" twins, avoiding their twinning law identification. Limited knowledge of the morphological, crystallographic, and optical characteristics of the twinning laws of gypsum was at the origin of this missed identification. Consequently, relatively little has been done to understand which impurities exert a critical role in the selection of different twinning laws and how this may impact our awareness of their occurrence in nature. Hopefully, to date, the crystallographic growth directions of the twinning laws of gypsum have been described, and their twinning energies have been determined (Follner et al., 2002; Rubbo et al., 2012a, 2012b). Only five different twinning laws are possible for gypsum structure, and each twinning law is described by a contact and a penetration twin; hence, at least ten different twinned habits are possible (Fig. 2). Therefore, in this PhD thesis, which largely represents the results described in Cotellucci et al. (2023a) and Cotellucci et al. (2023b), we provided new and useful tools to recognize the different twinning laws of gypsum univocally (Cotellucci et al., 2023a): the re-entrant angle value (θ), the extinction angle (Δ) formed between the two sub-crystals composing the twin, and the orientations of the primary fluid inclusions of the negative crystal shape (FIs) with respect to the twin plane (Fig. 2).

Despite this theoretical morphological variability, to date the 100 contact twinning law is the only well recognized gypsum twinning law occurring in natural environments (Ortí, 2010), whereas it has never been observed by laboratory experiments. Noteworthy, we suggested that the 101 contact twinning law occurs in geological evaporitic environments and has been confused with the most widespread 100 contact twin, up to date (Cotellucci et al., 2023a) (Fig. 3). Both 100 and 101 twinning laws show the same re-entrant angle value. However, the

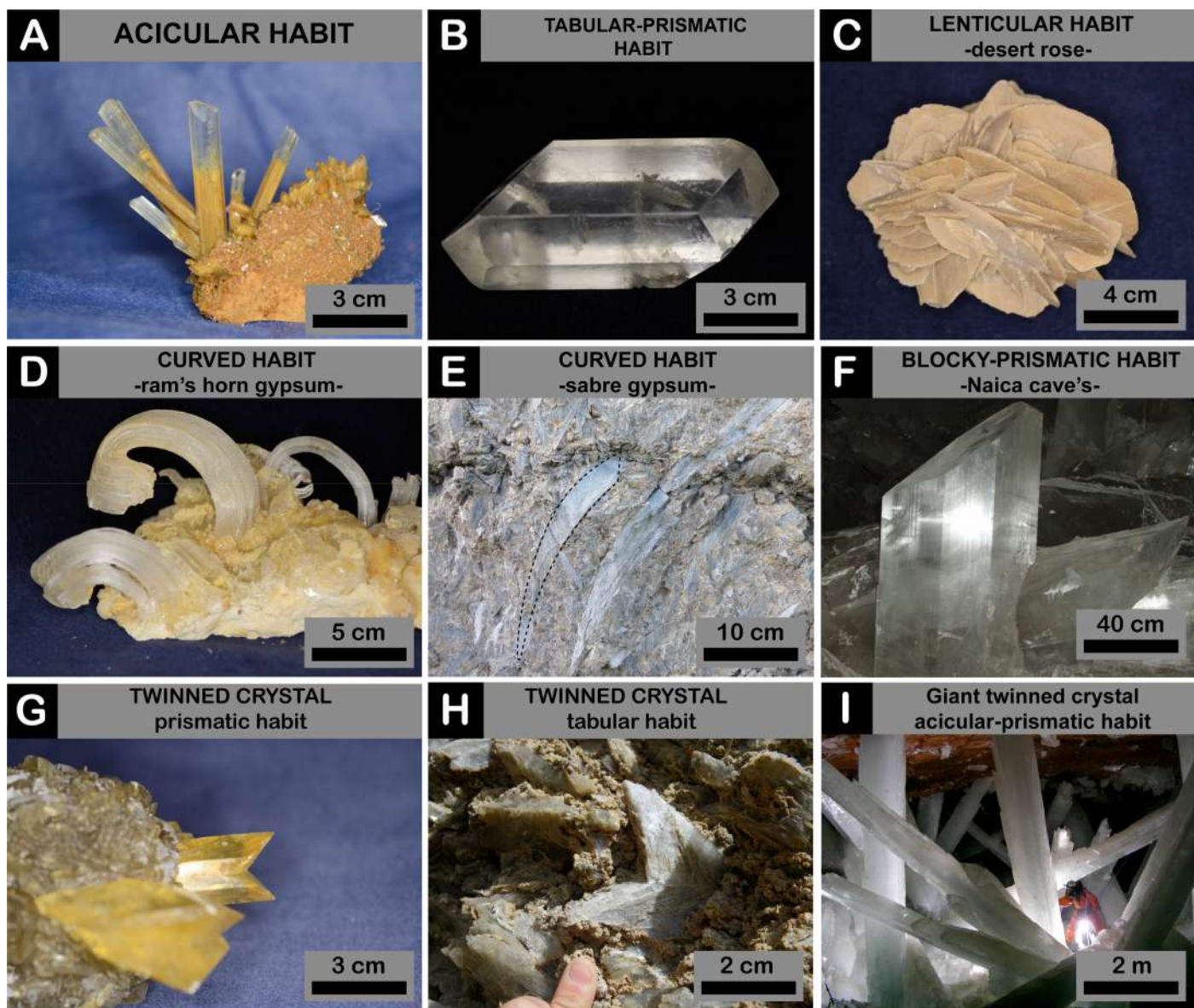


Figure 1 a) Acicular habit from Mexico, Naica (collection of the Turin Natural Science Regional Museum). b) Tabular-prismatic habit from Chaine Lake, Alberta, Canada (collection of the Turin Natural Science Regional Museum). c) Lenticular crystals aggregated together to form the well-known “desert rose” (from Tunisia; collection of the Turin Natural Science Regional Museum). d) Ram’s horn gypsum from Sicily, Cava di Rocca Chi Parra (collection of the Turin Natural Science Regional Museum). e) Curved gypsum crystals (sabre gypsum) from the Badenian succession of Poland. f) Blocky-prismatic single crystal from Mexico, Naica (ph. Juan-Manuel Garcia-Ruiz). g) Prismatic twinned crystal from Red River Floodway, Winnipeg, Manitoba, Canada (collection of the Turin Natural Science Regional Museum). h) Prismatic twinned crystal from Spain, Sorbas (ph. Laura Sanna). i) Giant acicular-prismatic twinned crystals from Mexico, Naica (ph. Laura Sanna - LaVenta archive).

sub-crystals composing 100 twins grow parallel to the twinning plane (Otálora & García-Ruiz, 2014), whereas we demonstrated that in 101 twinning law the main elongation of subcrystals is oriented obliquely with respect to the twinning plane (Fig. 3). Therefore, we also propose that the main elongation of the sub-crystals forming the twin with respect to the twinning plane is a useful tool to distinguish between 100 and 101 twinning laws, especially for natural samples whose optical extinction angles can often be difficult to measure.

Furthermore, we re-investigated gypsum habits in an impurity-free system by the evaporation of a solution saturated in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, focusing on the identification of twinning laws and their habit description (Cotellucci et al., 2023b): depending on the evaporation rates, acicular crystals, curved ones, 100 penetration twinning law, and 101 penetration twinning law can be observed.

Finally, the last chapter of the thesis analyzes the different gypsum habits observed both in presence and absence of sulfide oxidation. The preliminary results suggest that H_2S , along with its oxidation products, may promote the precipitation of 100 gypsum contact twin, and the possible geological implications of these laboratory experiments are discussed.

To summarize, in this thesis, i) we described which among the twinning laws of gypsum are possible in a pure solution and, for the first time, established a correlation between different gypsum habits and evaporation rates, so contributing to a better understanding of gypsum habits in evaporitic environments; ii) we provided new insights into the mineralogical implications of twinned gypsum crystals and their potential use as a tool for a deeper comprehension of the natural gypsum deposits; iii) we contributed to the debate on the origin

TWIN LAWS	CONTACT TWINS	PENETRATION TWINS	θ	Δ
100			105°	14°
$\bar{1}01$			105°	26°
001			132°	27°
20 $\bar{1}$			53°	24°
101			62°	43°

Figure 2 Geometrically, each twinning law is characterized by a specific re-entrant angle. By measuring its value, we can identify the twinning law. However, the $\bar{1}00$ and $\bar{1}01$ twinning laws have the same re-entrant angle (i.e., 105°). Thus, goniometry cannot distinguish these twins and the formal way to correctly identify the $\bar{1}00$ and $\bar{1}01$ twinning laws requires the measurement of the extinction angle (Δ) formed between the two individuals, by means of optical microscopy in crossed polarizers. This angle is 14° and 26° for $\bar{1}00$ and $\bar{1}01$ twinning laws, respectively. Moreover, Fls in $\bar{1}00$ twinning law are elongated along $[001]$ oriented parallel with respect to the twinning plane, whereas Fls in $\bar{1}01$ twinning law are always elongated along $[001]$ but oriented obliquely with respect to the twinning plane. Consequently, the orientations of Fls with respect to the twinning plane is a fast and useful method to distinguish between the $\bar{1}00$ and $\bar{1}01$ twinning laws. Modified from Cotellucci et al. (2023a).

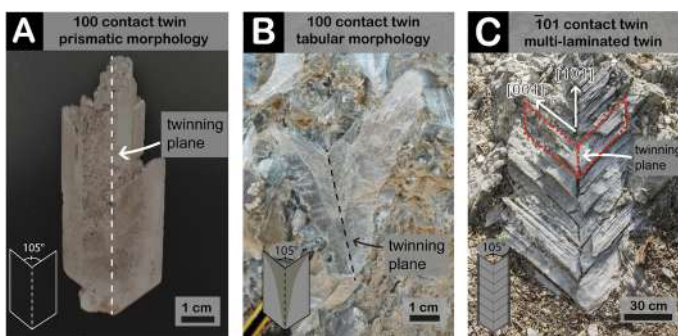


Figure 3 Examples of natural gypsum contact twins in modern and ancient evaporitic environments. **a)** Centimeter-sized gypsum twin from the Atacama Desert, Chile. **b)** Centimeter-sized Messinian selenitic gypsum from Piedmont basin, Italy (photograph courtesy of Marcello Natalicchio). **c)** Meter-sized Messinian selenitic gypsum from 'Vena del Gesso Romagnola', Italy, composed of many sub-crystals obliquely elongated with respect to the twin plane (photograph courtesy of Piero Lucci). Credits by Cotellucci et al. (2023a).

of ancient Salt giants, where 100 gypsum contact twins constitute a typical mineral component, providing new experimental data and stimulating further research in the field of the sulfur cycle in sedimentary environments. Our results improve the knowledge of the influences of variations in solution composition on the habits of gypsum crystals. This may aid in understanding the chemistry of the original brine in ancient sedimentary successions depending on the twinning laws of gypsum observed and their habits.

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Origin of 'ultra'-rocks

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INTRODUCTION

After decades of studies, it seems generally accepted that the Earth's mantle cannot be characterized by a homogeneous composition, either from a mineralogical, geochemical and isotopic point of view. It would rather be affected by re-fertilization and metasomatic processes in addition to continuous melt extraction, mostly along mid oceanic ridges. Indeed, the constant subduction and the recycling of crustal material, either continental and oceanic, necessarily causes selective enrichment of the previously depleted peridotitic mantle, resulting in an irreversible chemical and mineralogical heterogeneity (Stracke, 2021). This is clearly reflected in the variegated igneous lithologies characterised by a wide chemical compositional range. In particular, partial melting of veined lithospheric mantle sources may explain the presence of exotic liquids, whose formation cannot be ascribed to a classical four-phase mantle assemblage (Foley, 1992). Indeed, Davis et al. (2011) demonstrated that low degrees partial melting of a volatile-free Iherzolite source, which did not undergo any metasomatic events, cannot lead to the generation of melts with total alkali content higher than 3-4 wt.%.

Despite the rocks produced by these exotic melts have always attracted the attention of the scientific community, many rare lithologies continue to be a matter of discussion, and the characterisation of their mantle sources, and even their classification and nomenclature continue to be poorly constrained. A detailed and systematic study of these debated rocks might allow reaching a better knowledge of the mantle conditions, i.e., its thermal and chemical state, and of the processes responsible for their formation.

The goal of this thesis is to gain a deeper understanding of different groups of exotic and peculiar lithologies, mainly ultrabasic to basic, ultramafic and/or ultra-alkaline in composition, through a multidisciplinary investigation, based on petrographic, mineral chemical (SEM-EMP analyses), whole-rock geochemical data, together

with isotopic analyses (either on radiogenic systematics, as Sr-Nd-P, plus conventional, as C and O, and unconventional stable isotopes, as B) and petrological experiments at different pressure (from 1 to 5 GPa) and temperature (from sub-solidus to supra-liquidus) conditions.

The exotic samples investigated in this study have been collected from many sampling sites in different continental settings. They have been chosen by selecting the most variable petrographic, geochemical and isotopic differences, with the aim of performing detailed comparisons to highlight similarities and differences helpful to constrain the mantle sources and the processes involved in their formation.

The three main rock-types that have been accurately analysed are carbonatites, ultramafic lamprophyres and kamafugites. In particular, carbonatite samples come from Uganda (Toro Ankole Volcanic Province or TA) and from western Germany (Eifel Volcanic Field or EVF); ultramafic lamprophyres are from eastern Antarctica (Beaver Lake); and kamafugite from south-eastern Brazil (Alto Paranaíba Igneous Province or APIP), central Italy (Intra-Apennine Province or IAP) and Uganda (TA). Together with these samples, minor melilitites (Montefiascone Volcanic Complex, central Italy), leucitite and nephelinite (TA) have also been studied.

CARBONATITES

Carbonatites are igneous rocks containing more than 50% of primary carbonates and less than 20% of SiO₂ (Le Maître, 2002).

Carbonatites have been largely reported in the Cenozoic volcanism of Germany, as in the Eifel Volcanic Field (EVF) and in the Kaiserstuhl Volcanic Field (e.g., Schmitt et al., 2010). EVF comprises a western and an eastern district, almost parallel to each other, counting ~340 emission centres (mostly scoria cones, plus rarer lava flows and maars). EVF eastern areas display prevalently evolved terms (as phonolite and syenite), with less common carbonatites and mafic lithologies (e.g., Schmincke,

2007; Schmitt et al., 2010). Here, the Laacher See volcano showed mostly explosive and caldera-forming eruptions, coupled with the emplacement of a very limited volume of potassic lava flows (Schmincke, 2007).

The pyroclastic deposits, with phonolite composition, host a heterogeneous cargo of plutonic ejecta. The most common among them show mafic to felsic compositions, while < 5% is carbonate-bearing. On the other hand, the EVF western district shows basic to ultrabasic and mafic compositions, rarer evolved rocks, and only one occurrence of carbonatites.

The study has been mainly focused on plutonic ejecta, with a variable carbonate content (from sövite to syenite-carbonatite mixed samples; Fig. 1), coming from the Laacher See volcano. A subordinate set of leucitite samples has also been studied to highlight an eventual genetic link. Geochemical compositions vary from almost silica-free and CaO-rich rocks, up to strongly ultrabasic (moderately enriched in CaO) or to silica-rich (and CaO-poor) terms.

All the collected data suggest an evolution process for the Eifel melts, mainly constituted by two stages. Evolution started from a parental magma with a composition

similar to an olivine-melilitite (as those found in the near volcanic provinces) or leucitite (as those found in the Eifel), through a prolonged fractionation of olivine, clinopyroxene and/or melilitite, plus oxides in the latest stage (Fig. 2).

Such fractional crystallization would have allowed the melts to reach a phonolite composition, then causing an unmixing process with the production of a melt enriched in SiO₂ but poor in CaO and CO₂ (crystallizing syenite) and a melt poor in SiO₂ and enriched in CaO and CO₂ (crystallizing alvikites and sövites; Fig. 2).

The large chemical compositional range of the studied rocks would be the results of either silico-carbonatite melts (produced by minor carbonatite liquids trapped in the silicate aliquot; Fig. 1) or mechanical mixing of different percentage of silicate (as syenite) and carbonatite rocks.

ULTRAMAFIC LAMPROPHYRES

The term ultramafic lamprophyres (UML) was coined in 1986 by Nicholas Rock to indicate ultramafic, potassic to ultrapotassic melanocratic to holomelanocratic silicaundersaturated compositions, containing phenocrysts and

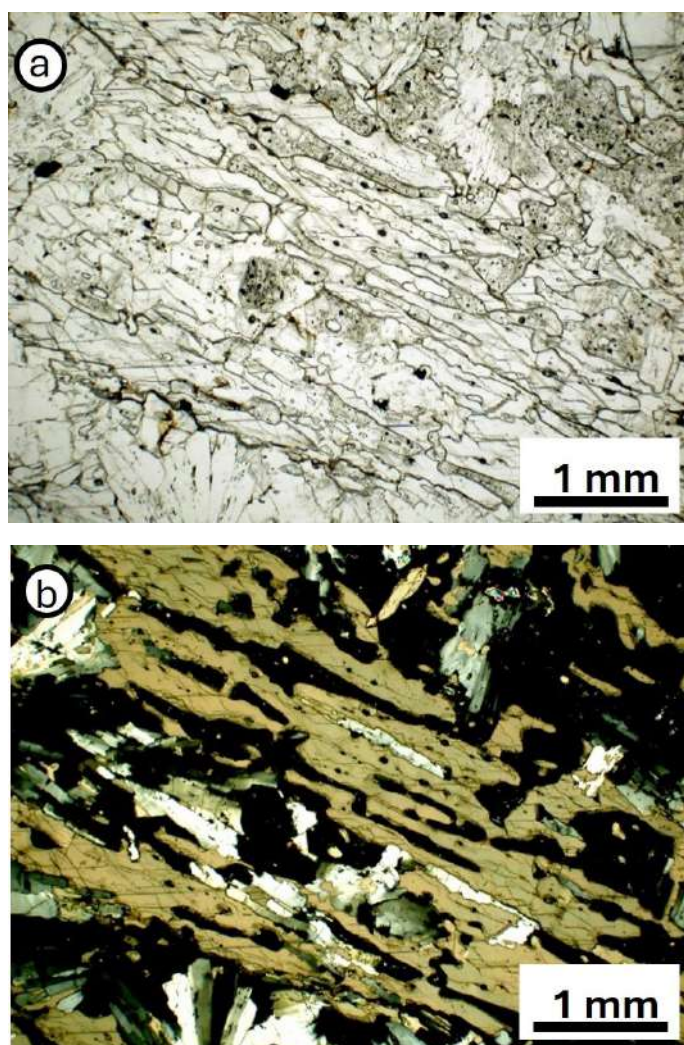


Figure 1 optical microscope micrographs of a calcite-bearing nosean syenite from Laacher See volcano a) plane polarized light; b) crossed polarized light.

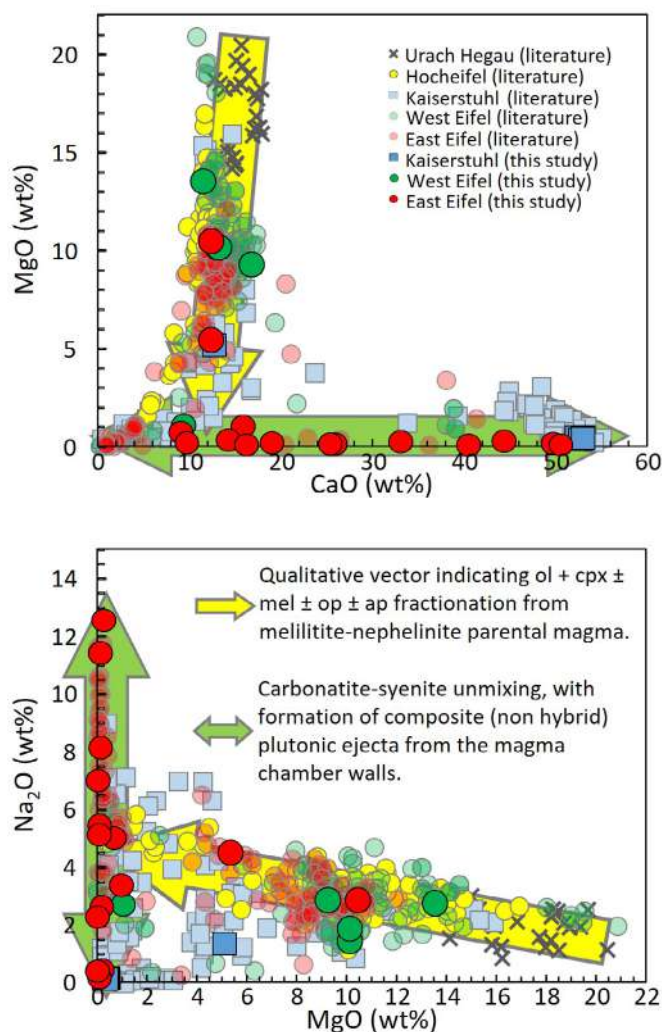


Figure 2 MgO vs. CaO and Na₂O vs. MgO Harker diagrams for EVF.

macrophenocrysts of olivine and phlogopite. UML represent another exotic igneous lithology with a still unclear classification, as the current IUGS classification includes only two UML types, grouped with the melilite-bearing rock (e.g., Le Maitre, 2002; Tappe et al., 2005).

Beaver Lake area is located along the Prince Charles Mountains, which mainly represent the East Antarctic Shield, Precambrian in age (e.g., Foley et al., 2006). The Beaver Lake area is part of the western flank of the Lambert-Amery rift, developed from Late Carboniferous during Mesozoic to Cenozoic (Foley et al., 2002; 2006).

The Beaver Lake UML products, emplaced in the Cretaceous (110-117 Ma), are represented by one dyke, two plugs (named the Konus and Novoe plugs) and two sills (named Radok-1 and Radok-2; Foley et al., 2002).

Petrographic and SEM-EDS analyses have been performed on three samples from the dyke, three from the plugs (two from the Konus Plug and one from the Novoe Plug) and four from the Radok-1 Sill. Major oxides and trace element data have been acquired for five of the most representative and less altered samples.

All samples (Fig. 3) are inequigranular and with $M > 90\%$, containing phenocrysts of olivine and microphe-nocryst or intergranular phlogopite, coupled with carbonate patches (here interpreted as a primary feature of the samples as they contain primary silicate phases). Therefore, samples must be classified as UML, and more specifically alnöite, as they also are melilite-bearing.

Among the analysed rocks, sill samples are potassic to ultrapotassic (K_2O/Na_2O ranging from 1.8 to 2.7), whereas the dike and the plug samples belong to the transitional series, having $K_2O/Na_2O < 1$. Although the K_2O/Na_2O ratios of the samples may have been affected by a post-emplacment alteration process, the sill samples are the most enriched in phlogopite, and potentially actually potassic to ultrapotassic, whereas dyke and plug samples show a phlogopite amount $< 5\%$ and probably an original much lower K_2O content.

The homogeneous petrographic and geochemical features of the samples point to similar petrogenesis, also supported by the spatial and temporal close relation. Minor differences recorded among the samples may be easily related to variable degree of partial melting.

The petrographic evidence, i.e., the presence of primary carbonate and the quite abundant K_2O -rich (as phlogopite) and Na_2O -rich phases (as nepheline; Fig. 3), together with the geochemical data, i.e., the very low silica content (33.0-35.9 wt.%) and the moderately high alkali content ($K_2O + Na_2O = 4.9$ -5.7 wt.%), may point to a source that is different from the classical peridotite mantle. It is generally accepted that the generation of melilite-bearing magmas is related to re-fertilized garnet-bearing peridotite, which has melted under vola-

tile-rich conditions (H_2O and, especially, CO_2 ; Dasgupta et al., 2006). Usually, the phase invoked to host hydrogen in the upper mantle is pargasite amphibole, which is stable up to a pressure of ~ 3 GPa (Foley & Pinter, 2018). As the depth of the Beaver Lake UML melts formation has been modelled to be higher than the spinel/garnet transition zone, at about 130 km (e.g., Foley et al., 2002), the presence of amphibole can be excluded. Instead, as phlogopite may be stable until 9-12 GPa (e.g., Pinter and Foley, 2018), it is therefore the best candidate to be in the UML mantle sources. About 15-30% of phlogopite would also guarantee the modest enrichment in K_2O content (1.5-3.3 wt.%) of the UML.

However, it is true that in two samples (dyke and plug rocks), Na_2O budget is higher than K_2O , and without amphibole to provide such element, clinopyroxene must be responsible for it. High modal contents of clinopyroxene in the mantle can be stabilized at the expense of orthopyroxene due to the infiltration of mobile carbonatite liquids in the wall-rocks (Yaxley et al., 1991). Sodic diopside can be produced by Na-rich dolomite liquids. Other than the presence of clinopyroxene, carbonatite metasomatism would guarantee the absence of orthopyroxene and the consequent low silica content of the melts, but also the CO_2 -rich conditions of the system.

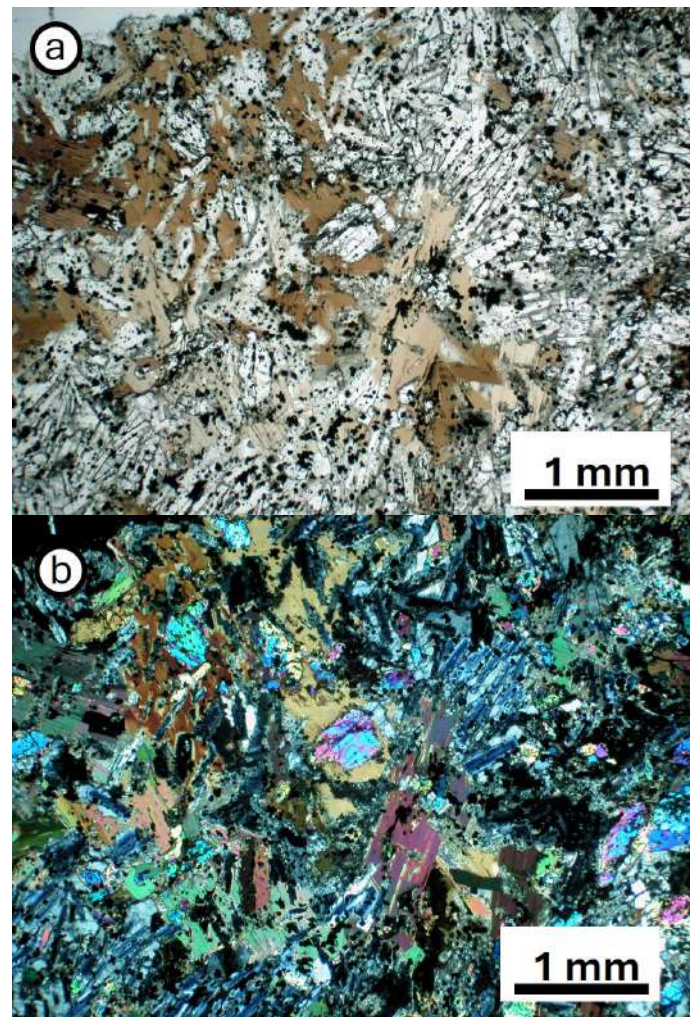


Figure 3 optical microscope micrographs of a UML from Beaver Lake, Radok-1 sill. a) plane polarized light; b) crossed polarized light.

Crustal recycling in the mantle beneath Beaver Lake area, as a consequence of the Antarctica and India collision (~1.1 Ga), could be responsible for the formation of metasomatic liquid in the UML sources. The formation of the Lambert-Amery Rift seems to be necessary both in its earlier stage for the production of exotic metasomes (phlogopite, clinopyroxene and carbonate) in the mantle and later for the melting events that generated the UML. Partial melting would have started from the metasomatic veins, which are characterized by a lower liquidus temperature, and eventually also involved the surrounding peridotite mantle.

KAMAFUGITES

The acronym kamafugite was coined by Sahama (1974), to refer to volcanic products with a silica-poor and alkali-rich (and with $K/Al > 1$) nature. The term kamafugite results from the initials of the names of three types cropping out in south-western Uganda, in Toro Ankole, along the western branch of the East African Rift System (i.e., KAtungite, MAFurite and UGandite).

Today kamafugite can be classified either according to its mineral (Le Maitre, 2002) or geochemical composition

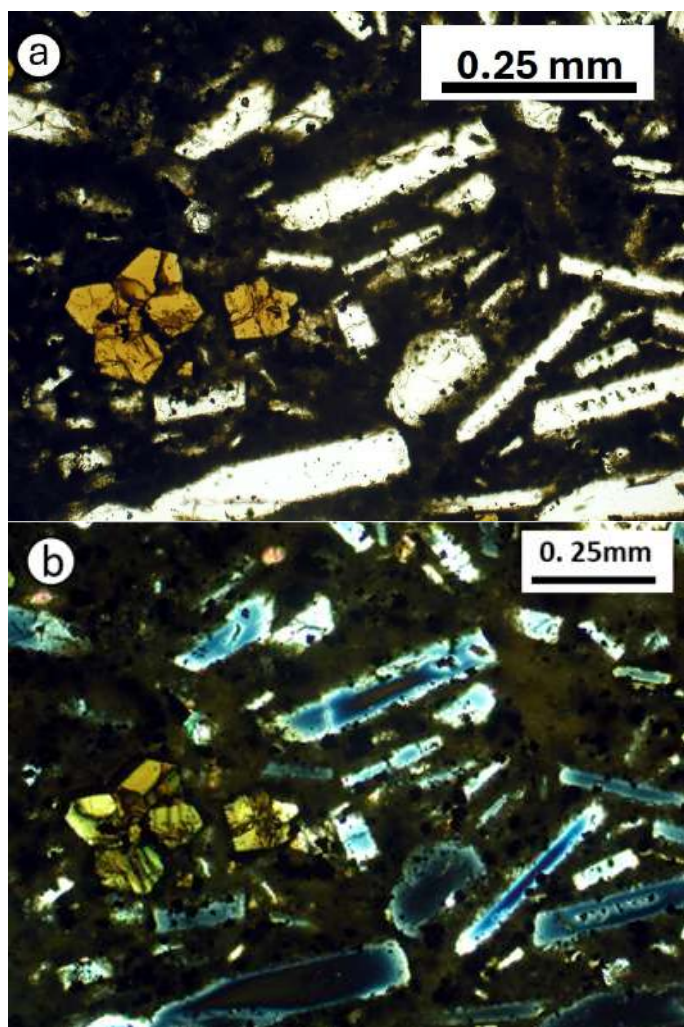


Figure 4 optical microscope micrographs of a porphyritic lava with euhedral microphenocrysts of melilite and perovskite, in a hypocrystalline altered groundmass. a) plane polarized light; b) crossed polarized light.

(Foley et al., 1987). Following the IUGS guidelines (Le Maitre, 2002), volcanic rocks characterized by the presence of primary kalsilite should be named kamafugite. Kamafugite rocks also represent the second group of ultrapotassic rocks (igneous products with K_2O and $MgO > 3$ wt.%; $K_2O/Na_2O > 2$), according to the classification of Foley et al. (1987). Kamafugite should be characterized by low SiO_2 content (< 46 wt.%), coupled with low Al_2O_3 and Na_2O , and strong CaO enrichment. The $Mg\#$ [$Mg\# = Mg/(Mg+Fe)$] should be > 60 (Foley et al., 1987).

Notwithstanding the existence of these two indications, the classification of kamafugites is still debated (e.g., Lustrino et al., 2020). The diagrams used by Foley et al. (1987) to discriminate the three ultrapotassic groups appear less appropriate in light of the new data that have been produced in the last 30-35 years. The IUGS guidelines have been recently questioned by Oliveira et al. (2022), highlighting the still confuse framework.

Until today, kamafugite rocks have been found in three worldwide localities only:

- Uganda, along the western branch of the East African Rift, and in particular in the northernmost and youngest volcanic province, Toro Ankole (TA; Uganda; Rosenthal et al., 2009). In TA, the volcanic activity started about 188 ka, and emplaced principally pyroclastic deposits, coupled with rarer lavas, often showing extreme compositions, as carbonatites, foidites, melilitites and kamafugites (Rosenthal et al., 2009; Innocenzi et al., 2024). These products embed exotic nodules, ultramafic in nature (from clinopyroxenite to glimmerite, with minor accessory phases as Ti-magnetite, apatite, perovskite and carbonate), interpreted either as mantle xenoliths or cumulate;

- Central Italy, in the Intra-Appennine Province (IAP), in San Venanzo and Cupaello (Lustrino et al., 2020). IAP (0.2-0.8 Ma) is an igneous district situated in the central Appennine Chain and composed of small monogenic to polygenic emission centres, probably developed as a consequence of the extensional faults of Plio-Pleistocene age. San Venanzo and Cupaello represent the type locality for two kamafugite endmembers (venanzite and coppaelite);

- South-eastern Brazil, in the Alto Paranaíba and Goiás Alkaline Province (Brod et al., 2005; Melluso et al., 2008). In particular, APIP is a Late Cretaceous and K_2O -rich province, probably related to an extensional tectonic regime. Intrusive bodies, pyroclastic products and lavas have been emplaced along the Neoproterozoic Brasília belt, with a composition varying between carbonatite, kimberlite, kamafugite, lamproite, dunite and alkali pyroxenite.

To these, we should probably add the Montefiascone Volcanic Complex (0.3-0.2 Ma), part of the Vulsini Vol-

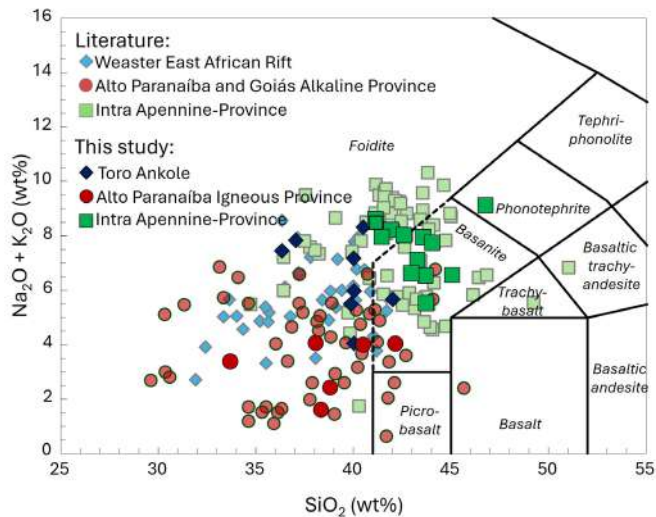


Figure 5 TAS diagram for the TA, APIP and IAP kamafugites, either from this study (bold symbols) and literature data.

canic District and the Roman Comagmatic Region (di Battistini et al., 2001). In this thesis, EMP analyses have been carried out on lava samples previously classified as leucite melilitite (di Battistini et al., 2001), highlighting the anhedral kalsilite crystals in their groundmass. Therefore, these samples should be reclassified as kamafugite, following the IUGS guidelines.

Kamafugites from the three provinces show similar parageneses, mainly differing in their olivine content, which ranges from less than 1% in Cupaello lavas (IAP) to 25% (San Venanzo products, IAP). Kamafugite samples are ultrabasic to basic, with a silica content of 33.7–46.8 wt.%, and show a variable enrichment in CaO (= 4.6–16.1 wt.%) and Na₂O + K₂O (= 1.6–9.1 wt.%; Fig. 5). Moreover, IAP and TA kamafugite have a potassic or ultrapotassic affinity (K₂O/Na₂O ranging from 1.8 to 9.0 in TA and from 7.3 to 24.1 in IAP). The K₂O/Na₂O ratio for APIP rocks is much lower (0.4–2.7).

While TA and APIP kamafugites share comparable budget for major oxides (e.g., Fig. 5) and trace elements (i.e., high TiO₂, from 3.6 to 5.8 wt.% in TA and from 3.6 to 6.4 wt.% in APIP, and MgO, from 6.4 to 22.2 wt.% in TA and from 13.5 to 20.5 wt.% in APIP), IAP counterparts often display different geochemical features (as lower TiO₂ = 0.7–1.1 wt.% and MgO = 9.9–14.0 wt.%). Kamafugite lavas from Uganda and Brazil also exhibit similar trace element enrichments and overlapping patterns on the Primitive mantle normalized diagrams, with negative peaks for K and P. On the other hand, Italian variants have deep trough for Nb-Ta, P, Ti and Eu, coupled with positive anomalies for Th, U, and Pb.

Radiogenic isotope analyses highlighted enriched values for all the provinces. ⁸⁷Sr/⁸⁶Sr isotopes ratios for TA and APIP, once again, is overlapping (~0.7056 and 0.7051–0.7057, respectively). IAP samples show the most radiogenic Sr values (0.7105–0.7113).

¹⁴³Nd/¹⁴⁴Nd values are generally lower in Brazilian kamafugite (0.51213–0.51227) than in Ugandans

(~0.512531), probably due to the older age of metasomatism. Again, the lowest values are related to IAP products (0.51200–0.51210). Pb isotope ratios are also slightly different (²⁰⁶Pb/²⁰⁴Pb ~19.40 in TA, 17.59–19.89 in APIP and 18.75–17.76).

δ¹¹B analyses have been conducted on IAP and TA lavas, as B is considered an effective tracker for mantle heterogeneities, and in particular crustal recycling (e.g., Agostini et al., 2021). δ¹¹B for TA kamafugites match well with mantle typical values (MORB from -6 to -8‰; OIB = -5 to -10‰; Agostini et al., 2021 and references therein) but the B ratios of the related lithologies, as glimmerite and clinopyroxenite nodules and carbonatites, reaches positive values, up to 6.6‰, highlighting altered oceanic crust ± marine limestone in the mantle source. IAP δ¹¹B (Cupaello = -7.6 to -7.9 ‰ and San Venanzo = -7.5 to -8.8‰) mainly overlap with the OIB range, with slightly lighter values that may point to sedimentary input in the mantle underlying central Italy.

The data suggest a metasomatized source involving carbonate, with similar mantle parageneses (phlogopite, clinopyroxene), suggested by the samples affinities. The heterogeneities highlight variable contributions to the melt from clinopyroxene and phlogopite in the three provinces, and different amounts of accessory phases, such as apatite and Ti/Fe-bearing opaques, that play a key role for melt compositions. Brazilian kamafugites require a slightly different source, with stronger contribution of olivine from the former lherzolitic mantle and/or a higher degree of partial melting.

Experimental study

As petrological studies provide further evidence to be combined with data from the natural samples, a set of near-liquidus experiments and a set of partial melting experiments on kamafugite have been carried out.

Near-liquidus experiments were carried out on four of the most representative and less altered kamafugite samples (one from TA, one from APIP and two from IAP, both from San Venanzo and Cupaello). Minerals resulting from the experimental runs should be in equilibrium with the melts and should represent the main phases of the kamafugite sources. Indeed, chosen samples have Mg# > 60 (considered the reference value for primitive exotic melts; Foley, 1999) and show no fractionation trend among the studied compositions. Moreover, petrography highlighted no or very few xenoliths and cumulate. Therefore, they represent the best approximation of the real melts.

Experiments support the idea of quite similar mantle sources for the three volcanic provinces, with a paragenesis different from the classical peridotite. A total lack of orthopyroxene has been recorded, while phlogopite

and clinopyroxene are abundant in all four experimental runs.

Compositional heterogeneities recorded among the worldwide kamafugites are reflected in the experimental results, which highlight a variable modal amount of phlogopite and clinopyroxene in the different mantle sources. For TA and APIP, the source composition is probably a phlogopite-rich (TA = 30-40% and APIP = 20-30%) clinopyroxenite, while for IAP a glimmerite hosting 40-50% of clinopyroxene. Olivine is found as a liquidus phase only in APIP (10-20%) and SAV (10%) runs, justifying the higher MgO contents.

Experimental results also outlined variable abundances of different accessory phases in the four samples. SAV runs show no minor phases, whereas in all the other experiments, apatite and Ti- and Fe-rich oxides are quite common. The mantle underlying Toro Ankole is probably the most enriched in accessory phases (3% of apatite, 4% of titanite and 5% Ti-magnetite). APIP mantle source probably hosts 2% of apatite and 5% of ilmenite (or Ti-magnetite).

Starting from these results, a possible source paragenesis has been reconstructed for the three provinces. The chosen compositions are: a phlogopite-bearing clinopyroxenite (with apatite, ilmenite, magnetite and titanite) for TA; an olivine clinopyroxenite (with phlogopite, apatite and ilmenite) for APIP; and to a clinopyroxene-bearing glimmerite (with apatite and magnetite) for IAP. Partial melting experiments were carried out at 2.7 and 5 GPa, reconstructing the conditions of the lithospheric mantles underlying the studied volcanic provinces, to test if the resulting melts actually match with the natural kamafugite. The resulting glass composition is influenced by the degree of partial melting (as temperature ranges from 1200 to 1550°C) and by the percentage of each phase that contributes to the melt.

Experimental glasses, for a partial melting degree from 20-30 to 70% (temperature = 1350 and 1400°C at 2.7 GPa, and = 1450-1550°C at 5 GPa), show an ultrabasic to basic, potassic to ultrapotassic and CaO-rich composition. MgO is generally quite high (up to 16.5 wt.%).

There is a quite good overlap between the glasses and the natural kamafugites compositions, in particular for Brazilian and Ugandan lavas.

Experiments demonstrated that slightly different degrees of partial melting of a clinopyroxenite (\pm olivine), variably enriched in phlogopite and accessory minerals (i.e., apatite, ilmenite and titanite) could represent the mantle source paragenesis of kamafugite magmas, also justifying the different features of the worldwide localities kamafugites.

MAIN IMPLICATIONS

All the analyses that have been carried out highlight the exotic nature of the samples. Petrography and mineral chemistry point out the presence of rare phases, as primary carbonate (found not only in the carbonatite samples, but also in the groundmass of kamafugites, ultramafic lamprophyres and melilitites), kalsilite, melilite and perovskite (diffuse in kamafugite, ultramafic lamprophyres and melilitite samples). Whole-rock geochemistry indicates strongly ultrabasic (carbonatites), ultrabasic (Ugandan and Brazilian kamafugite, ultramafic lamprophyres) and basic (Italian kamafugites) compositions, mostly characterized by a potassic to ultrapotassic affinity (K_2O up to 8.36 wt.% in Italian kamafugites, $K_2O/Na_2O < 24$). Moreover, all samples show a variable, but often marked, enrichment in trace elements. Also, the isotopic data indicates strongly radiogenic $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$, coupled with low values of $^{143}Nd/^{144}Nd$ isotopic ratios. Only two carbonatites represent an exception, having $^{87}Sr/^{86}Sr < BSE$ (present-day Bulk Silicate Earth). $\delta^{11}B$ values roughly fall in the mantle range (-8.3 to -3.3‰; Agostini et al., 2021), except for a few Ugandan rocks, having heavier values ($\delta^{11}B = -1.9$ to 6.6‰).

Even if samples cover a large compositional spectrum, multi-stage refertilization events must have occurred and must have strongly modified all the lithospheric mantle sources. Recycling of various lithologies, as marine limestone, caused by more or less old subductions, could explain either the carbonated metasomatism, necessary in all the analysed volcanic districts, but also the phlogopite and diopsidic clinopyroxene-rich veins, necessary in the formations of kamafugites, ultramafic lamprophyres and melilitites.

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A fluid and melt inclusion study of Fogo volcano, Cape Verde archipelago

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INTRODUCTION AND STATE OF THE ART: OIB VOLCANISM

Volcanic degassing is one of the key geological processes that permit the exchange of volatiles (e.g., H₂O, CO₂, H₂S, SO₂, CH₄, Cl, F) between the Earth's interior and its surface (Oppenheimer et al., 2014; Aiuppa et al., 2017, 2019; Plank & Manning, 2019). The release of volcanogenic volatile species can drive change in the atmosphere over timescales of millions of years (Oppenheimer et al., 2014; Plank & Manning, 2019). A comprehensive understanding of the pre-eruptive volatile contents in magmas is also critical for volcano motoring, hazard assessment, and risk mitigation. Gas exsolution has been acknowledged as a critical driver of rapid magma ascent and eruptions (Edmonds & Wallace, 2017). A proper understanding of initial dissolved volatile contents in mantle-sourced magmas is challenged by degassing and differentiation experienced by magmas during their ascent to the surface (Lowenstern et al., 2003). Since erupted lavas/pyroclastic materials are then extremely volatile-depleted upon eruption, one way to indirectly study the initial volatile content in magmas is via the characterisation of fluid inclusions (FI), small volumes of fluid trapped within crystals during their growth from the fluid (Rodder, 1979), and silicate melt inclusions (MI), droplets of melt trapped during phenocrysts growth in the magma (Esposito, 2021), both the inclusions FI and MI, are entrapped in crystals from mafic volcanic rocks. Microthermometric analysis of CO₂-dominated FI provides valuable insights into the pressure, and hence depth, of pre-eruptive magma storage across multiple magma ponding levels (e.g., Hansteen et al., 1998). Furthermore, noble gas and carbon isotope compositions of FI provide insights into the geodynamic evolution and composition of the mantle source, including the presence of mantle plumes (e.g., Gurenko et al., 2006; Day & Hilton, 2011; 2021; Rizzo et al., 2018; Sandoval-Velasquez et al., 2021). On the other hand, MI are studied to quantify the dissolved volatile contents at the *P-T-X* conditions of entrapment. Additionally, they enable the

determination of volatile contents in the parental melt if entrapment has occurred at or near the source (and before reaching volatile saturation) (e.g., Métrich & Wallace, 2008; Edmonds & Wallace, 2017). MI studies have been critical to estimating the abundance and distribution of volatiles in the Earth's upper mantle. Recent studies have revealed a C-rich signature of the mantle source of Oceanic Island Basalt (OIB) volcanoes (e.g., Longpré et al., 2017; Taracsák et al., 2019; Aiuppa et al., 2021). If the hypothesis suggesting the prevalence of carbon-rich OIBs globally holds true (e.g., El Hierro, Longpré et al., 2017; Taracsák et al., 2019; Piton de la Fournaise, Boudoire et al., 2018; Fogo, De Vitre et al., 2023), then OIB volcanism is expected to disproportionately contribute to the deep carbon flux into the atmosphere compared to volcanism in other settings, including Middle Oceanic Ridges (Dasgupta & Hirschmann, 2010; Hauri et al., 2019) and volcanic arcs (Plank & Manning, 2019). OIB volcanism opens a window into some of the more deeply explorable portions of the Earth's upper mantle (Hoffmann, 2003). Hence, quantifying the initial contents of volatile elements transported by such OIB magmas is crucial to understanding the cycling of volatiles from the deep planet interior (Hirschmann, 2006, 2018; Dasgupta and Hirschmann, 2010), and brings important clues on the roles of volatiles in mantle partial melting and magma generation and rise (Foley, 2011; Dasgupta, 2018). Unfortunately, however, the MI and FI dataset existing for OIB volcanoes is sparse and incomplete and biased toward a few better-studied volcanic systems such as Kilauea, Hawaii (e.g., Moore et al., 2015; Tuohy et al., 2016), Iceland (e.g., Hartley et al., 2014; Bali et al., 2018), and the Canary Islands (Longpré et al., 2017; Taracsák et al., 2019).

Cape Verde and Fogo volcano

One of the most active OIB volcanoes on the Earth is Fogo, in the Cape Verde Archipelago (West Africa) (Fig. 1). Previous studies on this volcano have provided insights into *i)* the architecture of the magma plumbing

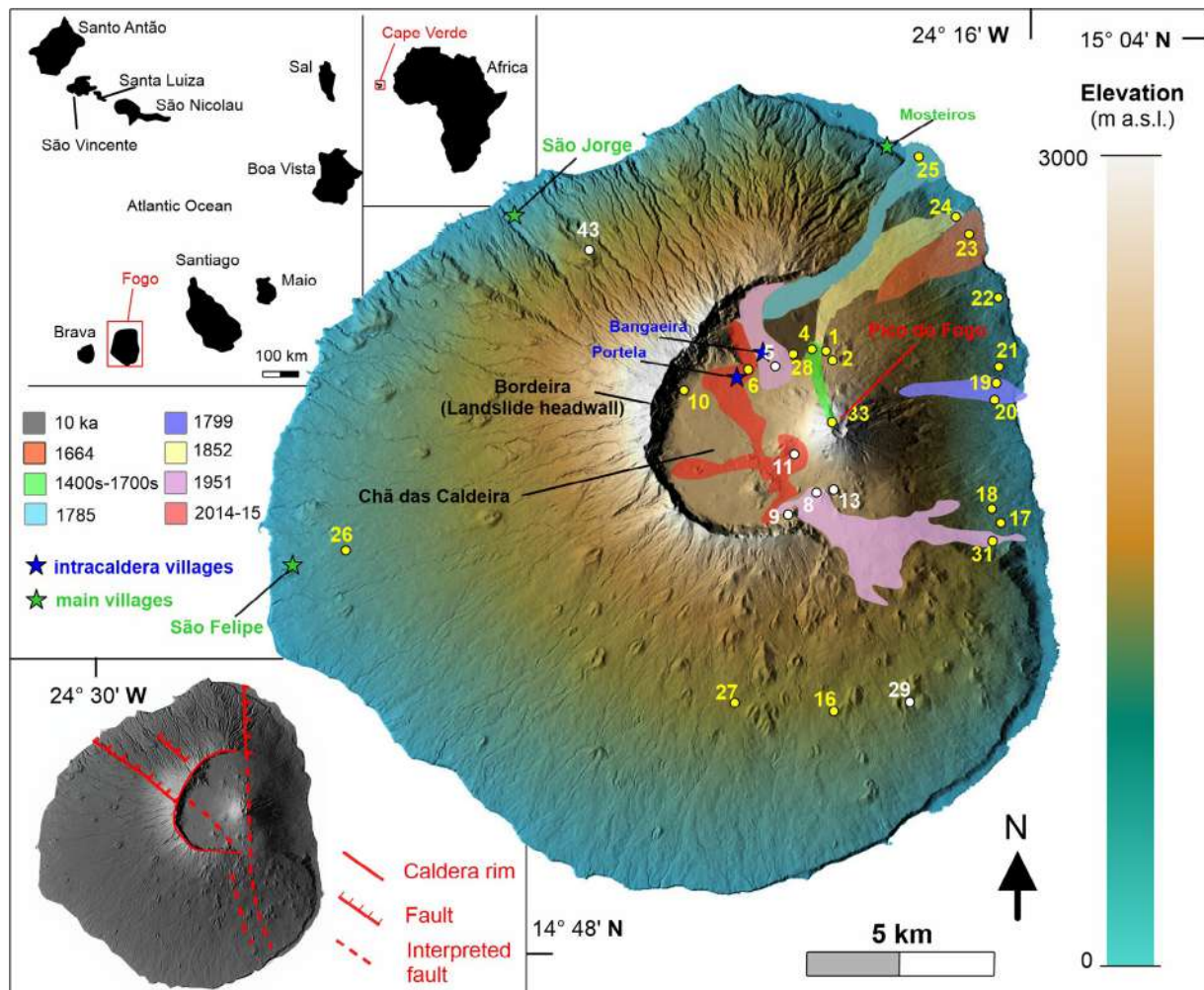


Figure 1 Digital elevation map of Fogo Island (modified from: Sketchfab website, managed by the Volcanology and Petrology lab's 3D models, Department of Geology and Geography, West Virginia University), showing sampling sites of lavas (yellow numbers) and pyroclastic deposits (white numbers). The studied eruptions are mapped from satellite images available from Google Earth and existing geological maps (Torres et al., 1997; Carracedo et al., 2015). Insets show the position of the Cape Verde archipelago (top, right), Fogo Island (top, left) and the main fault systems (bottom, left) (Day et al., 1999; Martínez-Moreno et al., 2018).

system (Klügel et al., 2020 and references therein); *ii*) the isotopic (Sr-Nd-Pb-He) composition of the mantle source (e.g., Christensen et al., 2001; Doucelance et al., 2003); and *iii*) the geochemistry of volcanic gases (Dionis et al., 2014; Aiuppa et al., 2020; Melián et al., 2021). In contrast, little information exists on the long-term stability or evolution of magma storage conditions (e.g., Hildner et al., 2011; 2012; Klügel et al., 2020) and on parental melt volatile contents and volatile evolution along the different regions of the magma plumbing system (DeVitre et al., 2023). Moreover, little is known about the factors that primarily control the isotopic diversity of the OIB mantle source, as well as the rates/modes of magma ascent prior to and during eruption.

RESULTS AND DISCUSSION

This study arises from the need to *i*) increase the actual limited knowledge on Fogo volcano and, more broadly, on the Cape Verde Archipelago and *ii*) provide new constraints useful for future assessment of volcanic risk at Fogo, where the latest eruptions (1951, 1995 and 2014/15) have proven catastrophic for local communities. Our novel data provide new constraints on the *i*)

vertical arrangement of the magma plumbing system beneath Fogo Volcano, from the deep crust/upper mantle to the surface, and its evolution over the last 120 ka of activity; *ii*) initial (parental melt) volatile contents, in the attempt to test the C-enriched source hypothesis and provide additional evidence for the C-enriched nature of alkali rich, OIB magmatism; *iii*) evolution of the lithospheric mantle source beneath Cape Verde archipelago, as well as, the occurrence of mantle metasomatism and/or refertilization events, and the recycling into the mantle of noble gases due to recent or fossil subduction.

The key findings of the FI microthermometry study are: *i*) a new conceptual model of the Fogo Volcano magma system, spanning the last 120 ka of activity; *ii*) the identification of two stable magma accumulation zones at ~25 km and ~13–21 km depth; *iii*) the identification of a transient, pre-eruptive magma stagnation zone at 9–12 km depth for magmas involved in the recent (last century) eruptions; *iv*) the rapid ascent, from 25 km depth, of magmas erupted in the early post-collapse phase (~60 ka), following a general reconfiguration of the plumbing system.

The main highlights of the MI study, carried out by combining Raman Spectroscopy, Nano-SIMS, Electron micro-

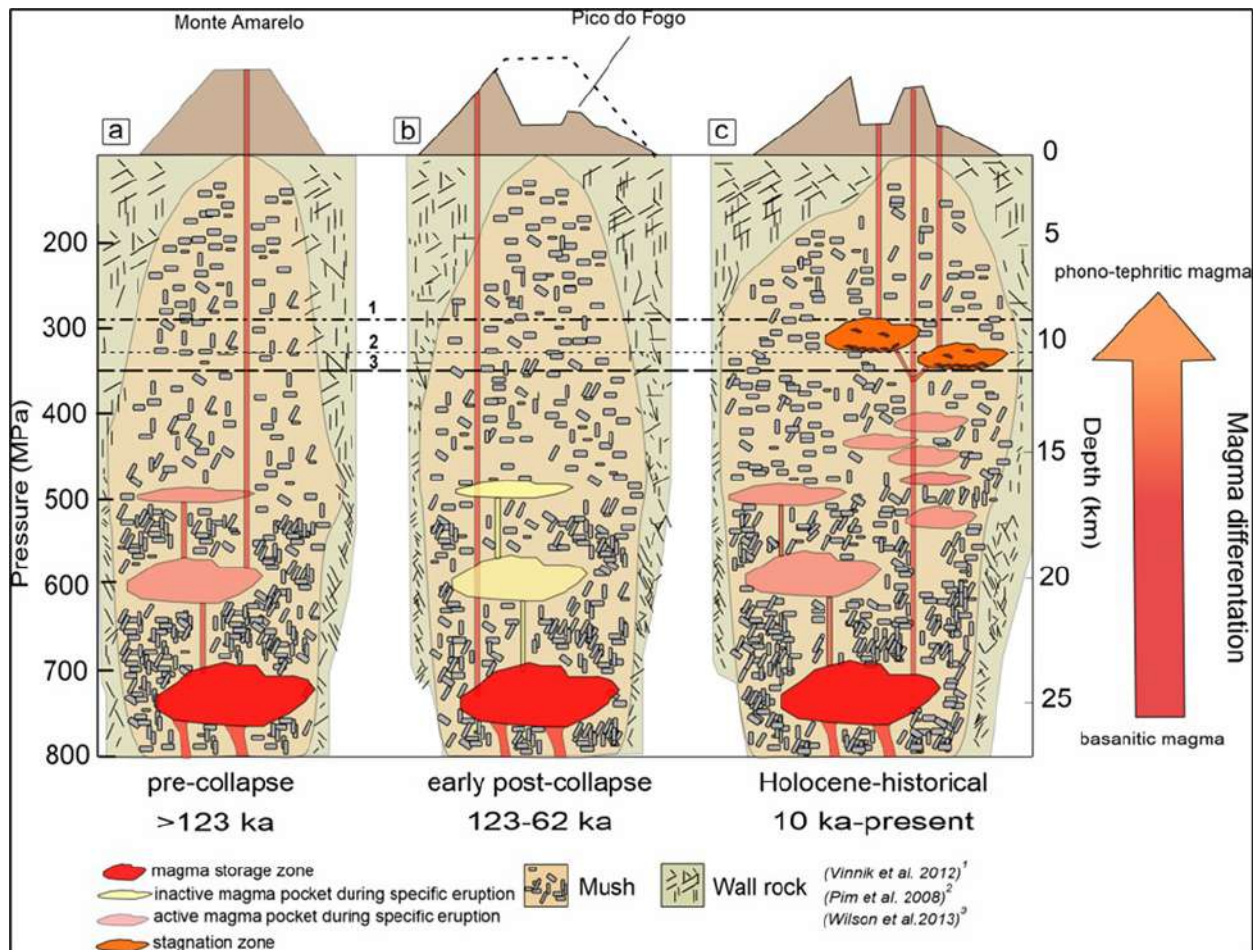


Figure 2 Schematic cross-sections of Fogo Island (not to scale), showing the temporal evolution of the magma feeding system during (a) pre-collapse, (b) early post-collapse and (c) Holocene/historical activity. FI in Holocene-historical eruptions suggest longer residence in a shallower magma ponding zone prior to eruption at the inferred fossil Moho (1) and/or at the upper mantle-crust transition (2,3). More evolved melts (e.g., phono-tephrites) may form in this region by fractional crystallization. The ~19 km and ~15-17 km regions are interpreted as parts of a vertically extended magma system, in which several interconnected ponding zones exist that are periodically refilled during specific eruptions. The main region of magma storage is at ~23.7 ± 0.9 km.

probe, and LA-ICPMS (chapter 6), are: *i*) mafic magmas feeding Fogo volcano are carbon-rich (2.1 wt. %); *ii*) a degassing model can reproduce the behaviour of volatiles (H₂O, CO₂, S, Cl, and F) during magma ascent/storage in the different magma plumbing system levels, and *iii*) the mantle source beneath Fogo exhibit extremely high carbon contents (up to 400 ppm). The characterization of the isotopic signature of carbon and noble gases in FI is discussed. The first carbon isotopic measurements in FI in the Cape Verde archipelago are illustrated and used to model the carbon isotopic evolution during degassing, from the mantle source to the surface. From this model, I predict a crustal signature for carbon in primary melts formed by upper mantle melting which is suggestive of mantle metasomatism by melts/fluids enriched in a crustal carbon component.

Temporal evolution of the Fogo volcano magma plumbing system, insights on fluid inclusion microthermometry

The architecture of the magma storage system underneath Fogo Volcano (Cape Verde Archipelago) is characterised using novel fluid inclusion results from fifteen

basanites, spanning the last 120 thousand years of volcanic activity, and encompassing a major flank collapse event at ~73 ka. Fluid inclusions, hosted in olivine and clinopyroxene, are made of pure CO₂ and, based on their textural characteristics, are distinguished in an early (Type I) and a late (Type II) stage. Inclusions homogenize to a liquid phase in the 2.8 to 30.8°C temperature range. Densities values, recalculated assuming an original 10% H₂O content at the time of trapping, range from 543 to 952 kg·m⁻³, and correspond to entrapment or re-equilibration pressure ranges of 500-595 MPa, 700-740 MPa, and 245-610 MPa respectively for pre-collapse, early post-collapse, and Holocene/historical eruptions. These entrapment pressures are interpreted as reflecting the existence of two main magma accumulation zones at ~25 km and ~13-21 km depth, and a zone of fluid inclusion re-equilibration at 9-12 km depth. There is evidence of a complex temporal evolution of the magma system. Historical eruptions, and especially the three most recent ones (occurred in 1951, 1995 and 2014-25), bring fluid inclusion evidence for transient, pre-eruptive shallow (9-17 km depth) magma ponding. Early post-collapse (60 ka) volcanics, in contrast, document fast magma trans-

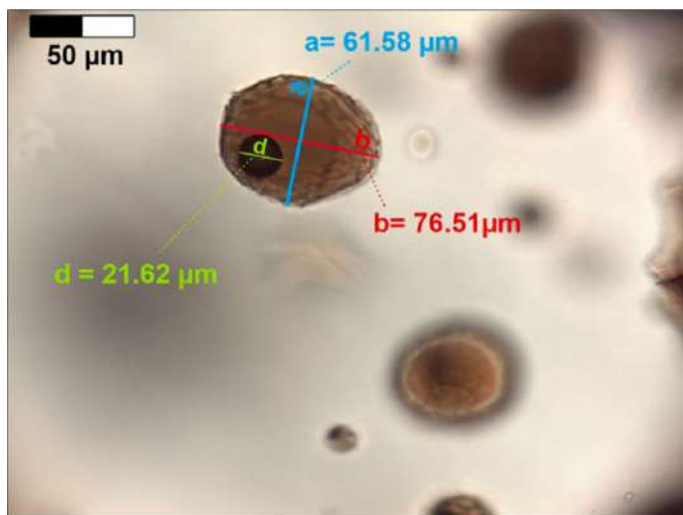


Figure 3 Measurements of the major (a) and minor (b) axes of the MI for the determination of the melt volume and measurement of the diameter (d) of the shrinkage bubble for the calculation of its volume.

port from ~25 km, and suggest a reconfiguration of the magma system after the Monte Amarelo collapse event (Fig. 2).

High CO₂ in the Cape Verde mantle source

Some of the most CO₂-rich magmas on Earth are erupted by intraplate ocean island volcanoes. Here, we characterise olivine-hosted melt inclusions (Fig. 3) from recent (< 10 ky) basanitic tephra erupted by Fogo, the only active volcano of the Cape Verde Archipelago in the

eastern Atlantic Ocean. We determine H₂O, S, Cl, and F in glassy melt inclusions and recalculate the total (glass + shrinkage bubbles) CO₂ budget by three independent methodologies.

We find that the Fogo parental basanite, entrapped as melt inclusion in forsterite-rich (Fo₈₀₋₈₅) olivines, contains up to ~2.1 wt.% CO₂, 3-47% of which is partitioned in the shrinkage bubbles. This CO₂ content is among the highest ever measured in melt inclusions in OIBs. In combination with ~2 wt.% H₂O content, our data constrain an entrapment pressure range for the most CO₂-rich melt inclusion of 648-1430 MPa, with a most conservative estimate at 773-1020 MPa. Our results, therefore, suggest the parental Fogo melt is stored in the lithospheric mantle at minimum depths of ~27 to ~36 km, and then injected into a vertically stacked magma ponding system. Overall, our results corroborate previous indications for a CO₂-rich nature of alkaline ocean island volcanism. We propose that the Fogo basanitic melt forms by low degrees of melting (F = 0.06-0.07) of a carbon-rich mantle source, containing up to 355-414 ppm C. If global OIB melts are dominantly as carbon-rich as our Fogo results suggest, then OIB volcanism may cumulatively outgas as high as ~16-21 Tg of carbon yearly, hence substantially contributing to the global deep carbon cycle.

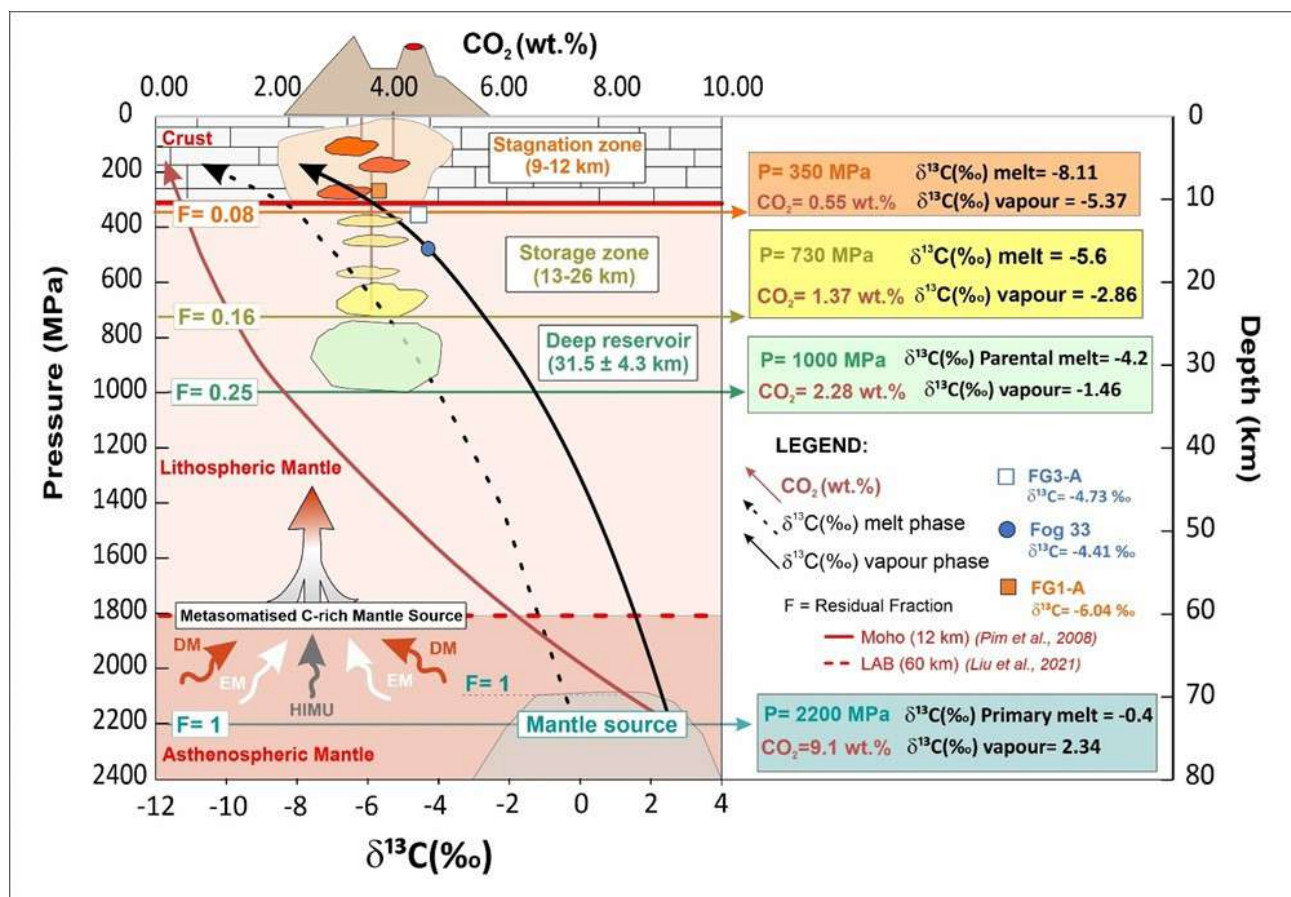


Figure 4 Conceptual model for CO₂ degassing in the Fogo storage system, illustrating the pressure-dependent evolution of (i) dissolved CO₂ in the melt (red line), (ii) δ¹³C in the melt phase (dash black line), and (iii) δ¹³C in the vapour phase (solid black line).

THE HELIUM AND CARBON ISOTOPIC SIGNATURE OF OCEAN ISLAND BASALTS: CLUES FROM FOGO VOLCANO, CAPE VERDE ARCHIPELAGO

Fluid inclusions (FI) entrapped in phenocrysts carried by Ocean Island Basalts (OIB) contain key information on volatiles' abundance and origin in their mantle sources. Here, we add a new piece of knowledge to our understanding of volatile geochemistry in global OIB magmas, by presenting new noble gas (He-Ne-Ar) and carbon (C) isotope results for olivine- and clinopyroxene-hosted FI from enclaves, lavas, tephra and volcanic gas samples from Fogo, the only frequently active volcano at the Cape Verde archipelago (eastern Atlantic Ocean). FI, together with crater fumaroles, constrain the Fogo $^3\text{He}/^4\text{He}$ signature at $7.14\text{--}8.44 \text{ Rc/Ra}$ (where Rc is the air-corrected $^3\text{He}/^4\text{He}$ isotope ratio, and Ra is the same ratio in air), which is within the typical MORB (Mid-Ocean Ridge Basalt) mantle. The carbon isotopic ratio ($\delta^{13}\text{C}$ vs. Pee Dee Belemnite) of CO_2 in FI and fumaroles ranges from -6.04 to -4.41‰ . We identify systematic variations of $\delta^{13}\text{C}$ and He/Ar^* with FI entrapment pressure (estimated from a combination of host mineral barometry and FI microthermometry), from which we develop a model for volatile degassing (Fig. 4) in the mantle-to-crustal magma storage system. The model predicts a crustal-like signature for carbon ($\delta^{13}\text{C}$ of $-0.4\pm 1.0\text{‰}$) in primary melts formed by mantle melting at $\sim 2200 \text{ MPa}$ ($\sim 77 \text{ km}$) and a source He/Ar^* ratio of $0.90\text{--}0.24$, which are indicative of variably depleted mantle metasomatized by carbon enriched melts/fluids from a crustal component. We also use our results to characterise regional (in the Cape Verde and Canary archipelagos) and global trends in C and He isotope composition from OIB. From a comparison with the few other OIB localities for which $\delta^{13}\text{C}$ are available, we propose that a carbon-enriched crustal component could be recurrent at a global scale in OIB magmatism, although often masked by isotope fractionation during magmatic degassing. We additionally find that, at the regional scale, He isotopes in the OIB scale inversely correlate with the degree of partial melting of the mantle beneath individual islands' (inferred from the La/Yb ratio of erupted basalts). More widely, our results corroborate previously established global relationships between OIB He isotopic signature, plume buoyancy flux and overlying plate velocity. In this interpretation, the MORB-like $^3\text{He}/^4\text{He}$ ($8\pm 1 \text{ Ra}$) at Fogo reflects a combination of (i) low to medium magma productivity, (ii) relatively low plume buoyancy flux ($\sim 1.1 \text{ Mg/s}$), and (iii) slow average velocity ($\sim 3 \text{ cm/yr}$) of the overlying plate.

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The Earth's interior redox state investigated through mantle xenoliths and mineral inclusions in diamonds: implications for large-scale magmatic events

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INTRODUCTION

The Earth's interior oxygenation (i.e., its redox state, f_{O_2}) is an important topic in mantle petrology and geochemistry due to its primary role in many processes occurring at depth, such as diamond formation, metasomatism, and partial (redox) melting. Variations in the oxygenation of the Earth's interior through time have been proposed to play a crucial role in the genesis and composition of mantle-derived primitive melts (Stagno & Fei, 2020), with consequent mobilization of C-O-H-S volatile elements in the form of CO_2 , H_2O , and SO_2 fluids. This, in turn, has affected the deep volatile cycle and chemistry of gases released during volcanic activity, which had a significant impact on the development of the terrestrial atmosphere and, importantly, the growth of life (Kasting & Catling, 2003; Scaillot & Gaillard, 2011). In addition, ascending oxidized fluids can also carry trace elements (e.g., Sc, V, Hg) with implications for their impact on the surface environments over time. The temporal evolution of the redox state is recorded by mantle-derived rocks through redox-sensitive minerals like spinel and garnet in xenoliths (peridotites and eclogites) or trapped in diamonds (Frost & McCammon, 2008). These minerals buffer the local f_{O_2} through the oxidation/reduction of Fe they host in the crystal structure. Terrestrial atmosphere and mantle seem to have experienced a simultaneous increase of O_2 through time (Stagno & Fei, 2020), linked by the onset of several geodynamical processes. For instance, the Great Oxidation Event (GOE) (2.5–2.0 Ga), and the Neoproterozoic Oxygenation Event (NOE) (1.0–0.8 Ga) coincided with the plate tectonics initiation, the continents formation and a large production of magmas (from komatiites to arc magmas and kimberlite blooms; Stagno & Fei, 2020 and reference therein). Oxidized CO_2 -rich melts that likely formed when an influx of oxygen from recycled material or upwelling of oxidized primordial material from the lower mantle interact with graphite or diamond (Frost et al., 2004; Wu et al., 2022) erupted between 250 and 50 Ma ago. During this period, large igneous provinces (LIPs) emplaced.

Large Igneous Provinces (LIPs)

The LIPs are characterized by terrestrial or submarine volcanism comprising enormous volumes of emitted lavas that emplaced within short time accompanied by wide-scale outgassing of CO_2 and SO_2 (Ernst & Bell, 2010; Black & Gibson, 2019) with a dramatic impact on the climate and environment. In fact, a temporal linkage exists between LIP events and the occurrence of the "big five" mass extinction and oceanic anoxic events (OAEs) of the Phanerozoic. Perturbations of C and S cycles triggered by large-scale volcanic eruptions (Jones et al., 2016) can be recorded in the coeval sediments worldwide distributed (Jenkyns, 2010) along with anomalous concentrations of mantle-derived trace elements like Hg (Yin et al., 2021), largely used as a LIP geochemical proxy in the sedimentary record (Grasby et al., 2019).

Aims of the thesis

The general objective of this thesis was to provide a link between the redox evolution of the Earth's mantle and the onset of large magmatic events. To have a comprehensive understanding of how Earth's interior f_{O_2} can affect the speciation and extraction of volatiles, I investigated the redox state of natural mantle rocks like spinel-peridotites (Marras et al., 2023a, b), Archean eclogites (Marras et al., 2024) and E-type diamonds, representative of different geological setting like continental lithospheric mantle and ancient subducted oceanic crust. The results allowed modeling the speciation of volatiles like CO_2 and SO_2 with respect to C and S and posing it as the cause of LIPs events. At this aim, the possible volcanic contribution was searched on sedimentary boundaries such as the Bonarelli level (~94 Ma), the diagenesis of which is synchronous to the large-scale volcanic activity of Caribbean, High Arctic and Madagascar LIPs.

RESULTS AND DISCUSSIONS

Hyblean mantle xenoliths (Sicily): a record of extensive oxidizing events involving S and C-species

Direct evidence of volatile mobilization at depth comes from fluid inclusions in silicate minerals like olivine, where the retained noble gases (He, Ar, Ne) can give information about their source. In this work, a suite of eight mantle spinel-peridotite xenoliths from the Valle Guffari (Hyblean Plateau, Sicily) was investigated to better understand the Hyblean mantle metasomatism and its redox evolution (Marras et al., 2023b).

Chemical and textural analysis were conducted by EMPA and SEM; $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in spinel was measured by both in situ synchrotron (beamline ID8, ESRF, Grenoble) and conventional ^{57}Fe Mössbauer spectroscopy (Sapienza University, Rome). Inclusions in olivine were studied by micro-Raman (Milano-Bicocca University, Milano), whereas OH bands were mapped by regular grids across olivine crystals (including inclusion trail regions) through micro-FTIR (beamline SISSI, Elettra, Trieste). Finally, noble gases isotopes (He, Ar, Ne) were analyzed from unaltered olivine grains by mass spectrometry (INGV, Palermo).

The calculated equilibration pressure (P) and temperature (T) of 0.9-1.2 GPa and 950-1050°C, respectively, along with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.27 and 0.31 measured in spinel, make Hyblean samples more oxidized than other peridotitic suites worldwide distributed from both cratonic and abyssal settings, with $\log f_{\text{O}_2}$ (with respect to

fayalite-magnetite-quartz buffer; FMQ) ranging between 0.28 and 1.27 (Fig. 1). Based on the $\log f_{\text{O}_2}$ vs $\text{Cr}^{\#}_{\text{spinel}}$ relationship proposed by Ballhaus et al. (1991), the samples fall in the lightly metasomatized xenoliths field, similarly to the metasomatized Vitim off-craton peridotites. At these redox conditions, coexisting C-O-H fluids (Fig. 1) consist of CO_2 and H_2O . The occurrence of microveins of silicate glass are taken as evidence of interaction with metasomatic fluids/melts. In addition, the fluid inclusions consist of Mg-Ca carbonates \pm sulfide \pm sulfur \pm CO_2 for the most reduced sample and Mg-Ca carbonates \pm Na-rich sulfates \pm CO_2 for the most oxidized sample (Fig. 1). This suggests that Na-bearing carbonatitic to carbonate-silicate melts are possible metasomatic agents. The chemical heterogeneity from the core to the rim observed in spinels (in particular, in terms of Cr_2O_3 vs Al_2O_3) and the high $\log f_{\text{O}_2}$ recorded with respect to the ambient lithospheric mantle (-2 to 0 ΔFMQ ; Fig. 1) are further evidence of a significant oxidation event that could have happened all at once or at several steps, controlled by the melt/rock ratio. The noble gases, along with the oxidized redox conditions, the geochemical evidence of interaction with Na- CO_2 -rich melts, the chemical composition of the analyzed inclusions (C-S-Na-rich), and the previous isotopic evidence of a sedimentary/organic C component in Hyblean peridotitic mantle (Correale et al., 2015), suggest the contribution of a slab-derived component. In conclusion, the lithospheric mantle beneath the Hyblean Plateau can be taken as an example of the role that metasomatic subduction-related CO_2 -rich silicate-bearing melts play in the oxidation of the lithospheric mantle and the mobilization of volatile elements.

First Fe^{3+} determination in spinel inclusions of olivine from a Mt. Vulture wehrlite

To date, the knowledge of redox conditions of spinel- and garnet-bearing peridotites is limited to lherzolite and harzburgite, where the application of the available oxy-thermobarometers requires the coexistence of spinel (or garnet), olivine and orthopyroxene. However, there are no available models to determine the f_{O_2} of wehrlites, orthopyroxene-poor or clinopyroxene-rich mantle rocks formed due to the interaction of a former lherzolite/harzburgite with metasomatic CO_2 -bearing silicate melts (Aulbach et al., 2020). This study (Marras et al., 2023a) was conceptualized with the goal of retrieving the f_{O_2} of the mantle beneath Mt. Vulture volcano (Italy) through the study of a wehrlitic lapillus emitted during the last eruption (~140 kyr ago), containing olivines with multiple tiny (< 40 μm) inclusions of spinel (Fig. 2a).

Here, for the first time, in-situ synchrotron Mössbauer spectroscopy (ESRF, Grenoble; Fig. 2b) was used to determine the Fe oxidation state of spinel inclusions in olivine (Fig. 2a), exploiting the high spatial resolution of the

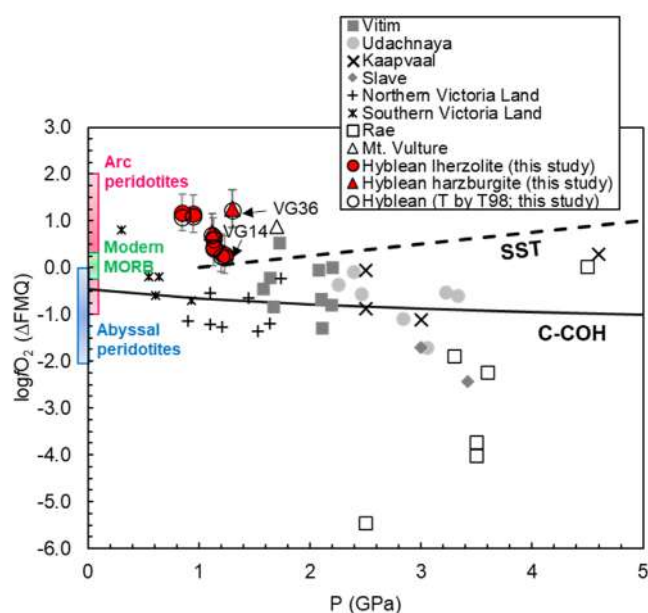


Figure 1 $\log f_{\text{O}_2}$ (ΔFMQ) plotted as a function of equilibrium P for Hyblean peridotites and literature samples (see references in Marras et al. 2023b). Reference values for MORB, abyssal and arc peridotites (Frost and McCammon 2008) are shown. The buffer C-COH (graphite/C-O-H fluids equilibrium; Ulmer and Luth 1991) is reported along with the sulfide-to-sulfate transition line (SST) from Chowdhury and Dasgupta (2020). Samples VG14 and VG36, the most reduced and the most oxidized samples, respectively, are indicated by arrows.

technique (area of $15 \times 6 \mu\text{m}^2$). Moreover, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ measurements of both spinel and host olivine were combined with chemical and spectroscopic analysis (micro-FTIR).

The determined $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for olivine range between 0.03–0.05 and for the entrapped spinels between 0.40–0.45. These ratios are higher than those reported in the literature for mantle spinel-bearing harzburgites/lherzolites. The calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ partitioning coefficient between olivine and spinel ranges between 0.06 and 0.13. The mantle origin of the trapped spinel inclusions was constrained by the absence of core-to-rim chemical variation, the absence of $\text{Mg}\#_{\text{spinel}}$ versus $\text{Fo}_{\text{olivine}}$ positive correlation related to liquidus minerals, and the consistency between the composition of the spinel inclusions and host olivine and those reported for orthopyroxene-bearing wehrlitic xenoliths from the same area.

Given the above evidence, it is proposed that the calculated f_{O_2} (0.8–1.0 ΔFMQ ; Fig. 1) likely records the interaction between a pristine spinel-bearing lherzolite and a CO_2 -rich metasomatic agent before spinels were trapped in olivines at mantle depths. Importantly, this investigation opens to the possibility of retrieving information about the f_{O_2} of mantle peridotites, even without spinel crystals in the rock matrix, by analyzing the $\text{Fe}^{3+}/\Sigma\text{Fe}$ and chemical composition of spinel inclusions in olivine, which allows reconstructions of the volatile speciation in the mantle.

Mineral inclusions in E-type diamonds from Siberian craton: witnesses of redox heterogeneities and eclogite as robust redox buffers

Subduction is the main carrier of oxidized material into the deep mantle and has a key role in changing the mantle redox state and controlling the volatiles (re)cycle (C, O, H, S, N, B) through time (Frost & McCammon, 2008; Stagno et al., 2019). Most kimberlite-borne mantle eclogites have been proven to be the product of metamorphic transformations that the oceanic crust (i.e., the protolith) undergoes during subduction into the subcontinental lithospheric mantle (Eskola, 1914; Ringwood, 1975). The study of eclogite xenoliths and more rare samples

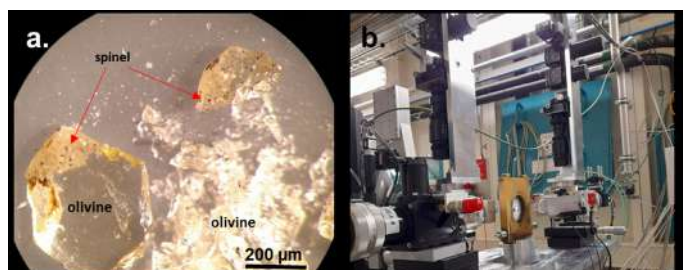


Figure 2 a) Mt. Vulture olivine grains with tiny ($< 40 \mu\text{m}$) spinel inclusions (black dots). b) Internal view of beamline ID18 of ESRF where in-situ synchrotron Mössbauer spectroscopy analyses were performed.

represented by mineral inclusions in eclogitic diamonds (E-type) allows reconstructing the ancient protolith nature and its redox evolution. Most eclogite xenoliths fall in the P - T field where diamond is thermodynamically stable and likely equilibrated with C-O-H fluids/melts. However, the primary redox state of these rocks could be masked by the interaction with circulating (metasomatic) oxidized fluids, which likely acted themselves as growth media for diamonds to form (Luth & Stachel, 2014). In this study, we investigated a suite of diamonds with E-type inclusions from the Siberian craton (Russia) to track the chemical and redox evolution of the subducted oceanic protolith, providing a model of diamond formations and the effect of metasomatism on the redox conditions of eclogites through time.

The coexisting garnet and clinopyroxene inclusions (Fig. 3), both exposed (after polishing) and trapped, have sizes ranging from 20 to 100 μm . The garnet and clinopyroxene hand-picked from the host eclogite of one diamond were also analyzed. The major elements and vanadium were measured by electron microprobe analyses on the exposed inclusions, while the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of both exposed and encapsulated inclusions was measured by in-situ Synchrotron Mössbauer spectroscopy (ESRF, Grenoble; Fig. 2b). Finally, the micro-Raman spectroscopy was employed to investigate additional tiny inclusions still trapped.

The compositions of garnet and clinopyroxene inclusions overlap with those for Udachnaya eclogitic xenoliths (e.g., Mikhailenko et al., 2020). Equilibrium T - P are 870–1170 (± 60) $^{\circ}\text{C}$ and 4.3–6.9 (± 0.4) GPa and are supported by Raman elastic geobarometry applied on a coesite inclusion observed in one of the studied diamonds. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet inclusions (0.02 to 0.07) and in clinopyroxene (0.11 to 0.20) is consistent with that measured on the eclogite host rock.

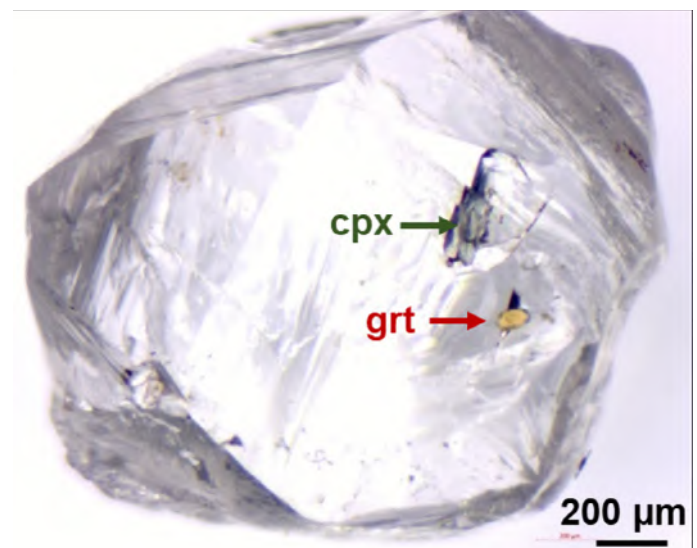


Figure 3 Eclogitic diamond from Siberian craton (this study) with coexisting clinopyroxene and garnet inclusions.

The bulk rock composition was reconstructed to constrain the nature of the subducted protolith for the eclogitic inclusions. Oxides like TiO_2 , Al_2O_3 , CaO and MgO (in wt.%) are typical of protoliths like peridotite-derived melts. The f_{O_2} of the convecting mantle source (i.e., f_{O_2} of the protolith) can be retrieved through the V vs MgO relationship, according to a recent study by Aulbach and Stachel (2022). In fact, we observed that V concentration acts as a robust proxy to retrieve the redox conditions of the protolith since it is not shifted by metasomatic processes occurring during eclogite residence in the cratonic mantle. The f_{O_2} of the eclogitic inclusions (i.e., the metamorphic minerals), calculated by Fe^{3+} -based oxy-thermobarometry, suggests that diamond formed from chemically diverse CO_2 - H_2O -bearing fluid/melt (with the contribution of CH_4). In conclusion, our data indicate that eclogites can buffer the f_{O_2} over aeons with a minor effect of metasomatism preserving, therefore, the conditions for diamond formation.

Evidence of a highly oxidized Archean subducted slab from V. Grib eclogites (NW Russia)

The f_{O_2} of eclogitic rocks is linked to the redox evolution of the oceanic protolith during subduction and residence in the lithospheric mantle. This allows modeling the speciation of volatile elements and the stability of diamond or graphite versus carbonate. Previous studies have shown that the f_{O_2} of natural eclogites varies significantly, ranging from -6 to -0.1 log units (ΔFMQ), related to the low Fe^{3+} content of garnets in eclogites, generally lower than 10%. Moreover, reconstructions of magmatic f_{O_2} (i.e., protolith redox conditions) from geochemical analyses of ancient unaltered eclogites and E-type diamonds (see above paragraph) suggest that Archean

mantle source conditions were reducing (Aulbach & Stagno, 2016).

Marras et al. (2024) investigated C-free mantle eclogites dated at 2.84 Ga from the V. Grib kimberlite pipe (Arkhangelsk Diamondiferous Province), one of the main diamond extraction sites in Russia. The Fe oxidation state of coexisting garnet and clinopyroxene was investigated by conventional Mössbauer spectroscopy (Bayerisches Geoinstitut, Bayreuth).

The equilibrium P and T for the V. Grib eclogites were found to be mostly within the diamond stability field, ranging from 3.0 to 5.2 GPa and 720 to 1050°C, respectively. The $\text{Fe}^{3+}/\sum\text{Fe}$ of garnet from five samples (between 0.03 and 0.20) exceeded the typical range reported for eclogitic garnets and correlated positively with the $\text{Fe}^{3+}/\sum\text{Fe}$ of clinopyroxene (0.18 and 0.38; Fig. 4). Consistently with what proposed for the Siberian eclogitic diamonds (see above paragraph), a major role of metasomatism for the oxidized conditions recorded by the V. Grib eclogites is excluded. Instead, we propose that the high f_{O_2} and bulk-rock $\text{Fe}^{3+}/\sum\text{Fe}$ were inherited by an oxidized magmatic protolith that implies the presence of an oxidized mantle source. In contrast to the reduced redox conditions recorded by Archean eclogitic xenoliths distributed worldwide, the V. Grib eclogites are the most oxidized eclogite rocks, and this might have contributed to the mobilization of C in the form of CO_2 , explaining the unusual C-free feature of these rocks.

This scenario is similar to the oxidized peridotite source proposed to explain the origin of picrites from the Emeishan LIP (Wu et al., 2022), which had significant implications for the release of large amounts of CO_2 to the atmosphere and, in turn, with the end-Capitanian mass extinction (~262 Ma ago).

A mineralogical, geochemical and isotopic study of the Bonarelli level (Gubbio, Italy)

Sedimentary rocks record paleo-environmental events that might have occurred at local and global scales. Among these, large volcanic eruptions throughout the Earth's history have driven sudden changes in the chemical composition of the terrestrial atmosphere and caused mass extinction. LIPs are known to be coeval to the Phanerozoic largest mass extinctions and the OAEs, characterized by strong perturbations of carbon and sulfur cycles. The identification of these global-scale events in the sedimentary record is made possible by using key geochemical signatures such as high organic matter content (up to 30%) and positive excursions in the $\delta^{13}\text{C}$ curve (Jenkyns, 2010). The Bonarelli level, a ~0.9-m thick layer made up of organic-rich shales, cropping out at the Valle della Contessa section in Gubbio (Italy; Fig. 5) within the pelagic limestones of the Scaglia Bianca For-

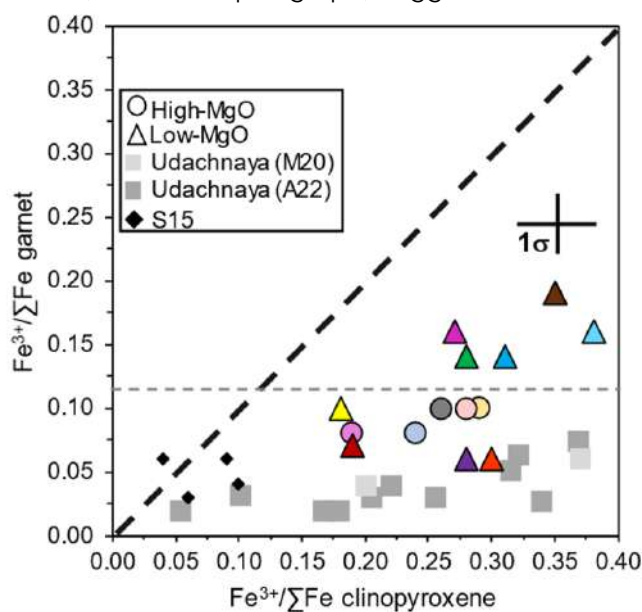


Figure 4 The $\text{Fe}^{3+}/\sum\text{Fe}$ in garnet and clinopyroxene from this study compared with values for natural eclogites from Udachnaya and synthetic samples (see Marras et al., 2024 for the references). The dashed grey line is the maximum $\text{Fe}^{3+}/\sum\text{Fe}$ reported in the literature for eclogitic garnets.

mation, is considered a stratigraphic marker of the OAE2 (Cenomanian-Turonian, ~94 Ma). This event was likely triggered by submarine volcanism of the High Arctic and Caribbean LIPs or subaerial volcanism of Madagascar LIP (Grasby et al., 2019 and references therein). Despite the extensive lithological, biostratigraphic, and carbon isotopic studies conducted on the selected section, a comprehensive investigation of the LIP signature in this locality is still needed and could benefit from the use of Hg concentration as a geochemical marker, combined with Hg, C, S and Sr isotopes.

In this study, X-ray diffraction, petrographic and geochemical (Total Organic Carbon, Hg concentration, trace elements, Hg, S and Sr isotopes) analyses on various samples collected from the Bonarelli level along with rocks samples from the Scaglia Bianca Formation were performed to explore the link between OAEs and LIP volcanism.

The results show that Bonarelli level mineral fraction is mainly composed of quartz, phyllosilicates, sulfates (barite and jarosite) associated with sulfides. Sharp anomalies of Hg were observed and correlated positively with chalcophile elements such as Cu, Ni and Fe and with the amount of sulfate/sulfide. Due to the affinity of Hg with the organic matter (Grasby et al., 2019), the Hg concentration was normalized to TOC (Hg/TOC). However, the collected samples show that the Hg signal is still preserved. The results from this study indicate that the Valle della Contessa section records an extra input of Hg released into the environment around 94 Ma ago. Integrating these data with Hg, S and Sr isotopic analyses, we observe a (deep) magmatic contribution for Hg that correlates with a slight positive shift of the sedimentary $\delta^{34}\text{S}$ isotopic signature toward mantle values, plus a continental origin for Sr related to huge weathering. In conclusion, we interpret our results as evidence of the LIP emplacement and large-scale CO_2 , SO_2 and Hg release.

FINAL REMARKS AND FUTURE PERSPECTIVES

The results of this multidisciplinary investigation have revealed novel information about the mechanism of mantle oxidation, the heterogeneous redox conditions of the upper mantle over time and space, as well as the crucial role of redox-driven processes in mobilizing volatiles, which have implications for sedimentary and biological processes on the Earth's surface. Furthermore, this study has raised new questions, some of which have been preliminarily addressed. Given the evidence of a mantle origin for the Hg released in the frame of LIPs, preliminary (and in progress) in situ synchrotron high-pressure and -temperature stability and liquid structure experiments were conducted on the sulfide Hg end-member, i.e., cinnabar (HgS), to understand the mechanism of Hg

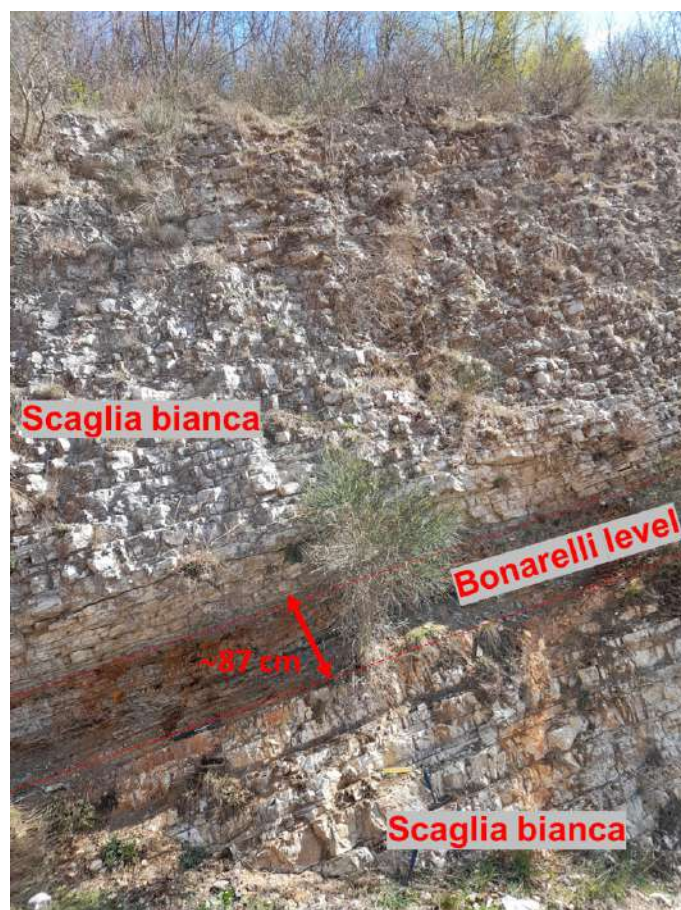


Figure 5 Stratigraphic section object of this study located in Valle della Contessa (Gubbio, Italy), where the black-shale Bonarelli level (dark; ~87 cm thick) outcrops with the micritic limestone Scaglia Bianca (grey).

mobilization from the mantle source. These experiments laid the groundwork for future solubility experiments of Hg in oxidized LIP-related melts, which are crucial for modelling the deep Hg cycle from the mantle to the atmosphere during large magmatic events.

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The geodynamic evolution of the Gondwana-Laurasia boundary in Triassic times

Constraints from the tectono-magmatic cycles of the Southern Alps

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INTRODUCTION

The Triassic geodynamic evolution at the Gondwana-Laurasia boundary in the area now corresponding to the Southern Alps has been a subject of debate in the last five decades. The Southern Alps (Fig. 1), located at the northern margin of the Adriatic Plate, was marked by the development of carbonate platforms and basins and widespread magmatic activity during the Triassic (e.g., Gianolla et al., 1998; Lustrino et al., 2019). The Triassic magmatism in the Southern Alps, largely studied in detail in the eastern sector (e.g., Dolomites, Vicentinian Alps, Julian Alps, etc.), occurred in two major cycles. The first cycle, from the Middle to early Late Triassic (~243-235 Ma), was characterized by the emplacement of volcanics and intrusions of high-K calc-alkaline to shoshonitic geochemical signatures (Bonadiman et al., 1994; Lustrino et al., 2019; Storck et al., 2019; De Min et al., 2020; Casetta et al., 2021). This was followed, in the Late Triassic to Early Jurassic (~230-190 Ma) by a magmatic cycle with geochemical affinities varying from alkaline to transitional and tholeiitic (Cassinis et al., 2008; Casetta et al., 2019; De Min et al., 2020). In the central (i.e., Brescian PreAlps) and western (i.e., Ivrea-Verbano Zone, IVZ) sectors of the Southern Alps, many details and datasets on the Triassic magmatic events are however unavailable (Cassinis et al., 2008; Stähle et al., 1990, 2001; Mazzucchelli et al., 2010; Schaltegger et al., 2015; Galli et al., 2019; Bonazzi et al., 2020; Giovanardi et al., 2020). Due to this situation and the widespread hydrothermal alteration of outcrops, substantive correlation of the magmatic events that occurred in the different sectors of the Southern Alps (at the Gondwana-Laurasia boundary) during the Triassic is currently lacking. The relation of these magmatic events of the Southern Alps to the geodynamic environment during the Triassic is also complicated and strongly debated, particularly with respect to the Middle Triassic magmatism exhibiting high-K calc-alkaline to shoshonitic affinity in contrast to the extensional to transcurrent tectonics (Doglioni, 1987; Bonadiman et al., 1994; Gianolla et al., 1998) which was prevalent during this time.

Hence, to provide further constraints on the geodynamic evolution of the Gondwana-Laurasia boundary in Triassic times prior to the breakup of the Pangea, this thesis documents the results of detailed petrological, geochemical and isotopic studies on the Triassic-Early Jurassic magmatic events which occurred in the Southern Alps, particularly in the westernmost (IVZ) and eastern (Dolomites) sectors (Fig. 1). The orogenic mantle massifs exposed in the IVZ were also studied to provide first-hand constraints on the nature and evolution of the possible mantle sources of the Triassic magmatism in this area.

Research objectives

The objectives of the research included:

- 1) Comparison of the tectono-magmatic evolution of the westernmost Southern Alps (Ivrea-Verbano Zone) with respect to the eastern (Dolomites) and central (Brescian PreAlps) sectors.
- 2) Detailed characterization of the poorly-studied Late Triassic tectono-magmatic events of the Southern Alps. In this frame, invaluable constraints were provided by the investigation of the deep intrusions in the Ivrea-Verbano Zone.
- 3) Provide new geochronological and isotopic constraints (U-Pb, Lu-Hf, Sm-Nd, Rb-Sr, Pb-Pb) on the Southern Alps tectono-magmatic events.
- 4) Determine the origin and nature of crustal components in uprising mantle melts in the Southern Alps.
- 5) Unravel the nature, heterogeneity, and evolution of the subcontinental lithospheric mantle beneath the Southern Alps. In this case, the study of the Ivrea-Verbano Zone mantle peridotites also provided unique insights.

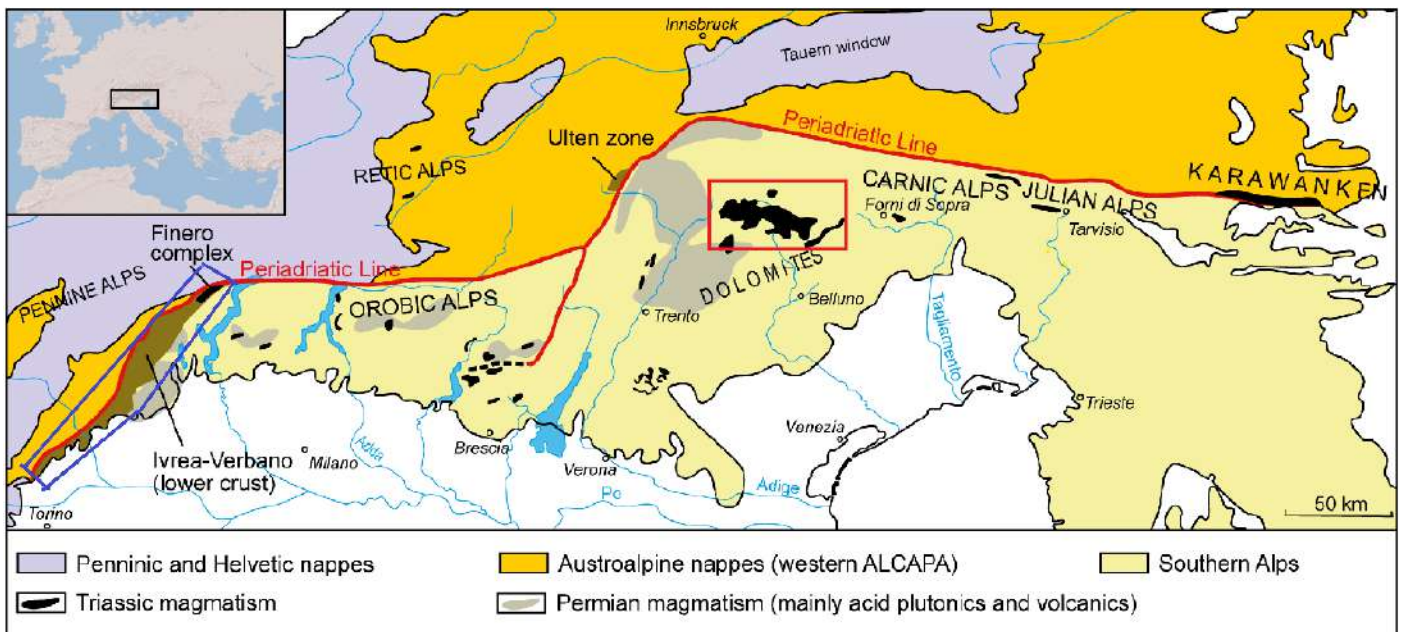


Figure 1 Generalized geological map of the Southern Alps (modified after De Min et al., 2020) showing the locations of the Ivrea-Verbanio Zone (marked in blue) and the Dolomites (marked in red), focus of the present research.

SAMPLE SUITES, PETROGRAPHY AND ANALYTICAL METHODS

From the northern part of the Ivrea-Verbanio Zone, western Southern Alps (Fig. 2), swarms of dykes of presumably Triassic to Early Jurassic ages, which intruded into the Finero Phlogopite Peridotite (FPP) massif, were sampled. These dykes range in composition from diorite to anorthosite, gabbro, and hornblendite, and sometimes contain cumulates of peridotite and clinopyroxenite. Detailed petrographic, mineral chemical, U-Pb zircon geochronology and Sr-Nd-Hf-Pb isotopic investigations were performed on these samples. Samples of the phlogopite-bearing harzburgite and websterite lithologies of the FPP were also collected and studied for their mineral and Sr-Nd-Hf-Pb isotopic composition.

In the central to southern parts of IVZ, lherzolitic massifs outcrop in Premosello, Balmuccia and Baldissero (Fig. 2). Samples of spinel-lherzolites, Cr-diopside pyroxenites and websterites were collected from these three massifs for mineral chemical and Nd-Hf isotopic studies.

The Dolomites in the eastern sector of the Southern Alps preserve abundant volcano-sedimentary sequences and plutonic complexes largely formed during the Middle Triassic (Fig. 1). Basaltic lavas and dykes from these Middle Triassic sequences were sampled. The samples were analyzed for their whole-rock, mineral chemical and Sr-Nd-Hf-Pb isotopic composition.

Geochemical, geochronological and isotopic characterizations of sampled rocks were largely focused on the analysis of mineral phases after detailed petrography in order to overcome the limitation imposed by the high degree of alteration of Triassic outcrops in the Southern Alps. The analysis of different generations of minerals and the systematic core-to-rim analysis also provided

the opportunity for unraveling and tracing geochemical changes recorded by the studied rocks.

RESULTS AND DISCUSSION

Transition from orogenic-like to anorogenic magmatism in the Ivrea-Verbanio Zone, western Southern Alps

The Ivrea-Verbanio Zone (Fig. 2) is an iconic upper mantle to lower continental crust sequence of the Adriatic Plate and represents a unique opportunity to investigate the tectono-magmatic events that occurred at the Gondwana-Laurussia boundary from Late Paleozoic to Early Mesozoic. New geochemical, U-Pb zircon geochronology and Sr-Nd-Hf-Pb isotopic data documented for alkali-rich dyke swarms which intruded the Finero Phlogopite Peridotite (northern IVZ) provide geological constraints on the nature, origin and evolution of Triassic-Early Jurassic magmatism in the Southern Alps. The studied dykes are amphibole- and phlogopite-bearing and show geochemical features varying between two end-member groups (Fig. 3a-b). A dyke group is characterized by HFSE-poor, Al-rich amphibole (Al_2O_3 up to 16 wt.%) with high LILE and LREE contents, high radiogenic $^{87}\text{Sr}/^{86}\text{Sr}_{(t)}$ (0.704732 to 0.704934) and low radiogenic Nd isotopes ($\epsilon\text{Nd}_{(t)}$ from -0.1 to -0.7) (Fig. 3). The composition of this dyke group points to an "orogenic-like" affinity, and is very similar to the composition of Middle Triassic lavas from the Dolomites (Fig. 3b; Lustrino et al., 2019; De Min et al., 2020; Casetta et al., 2021) suggesting that dykes of this group (which are all zircon-free) may be of Middle Triassic age. The mineralogy, trace elements and Sr-Nd-Hf-Pb isotopic composition of these dykes suggest segregation from evolved mantle melts containing significant amounts of recycled continental crust com-

ponents. This dyke group was interpreted to have been largely derived from metasomatized lithospheric mantle sources.

The second group is HFSE-rich with Al-poorer amphibole enriched in LILE and LREE, low radiogenic $^{87}\text{Sr}/^{86}\text{Sr}_{(t)}$ (0.703761–0.704103) and higher radiogenic Nd isotopes ($\epsilon\text{Nd}_{(t)}$ from +3.4 to +5.4) pointing to an “anorogenic” alkaline affinity and asthenospheric to deep lithospheric mantle sources (Fig. 3a-b). Zircons from dykes of this group show concordant $^{206}\text{Pb}/^{238}\text{U}$ ages varying from 216 ± 9 Ma to 191 ± 10 Ma (Late Triassic-Early Jurassic). The highly variable $\epsilon\text{Hf}_{(t)}$ values (+15.4 to -0.4) measured in situ on zircons from these dykes point to the heterogeneous, variably depleted nature of their asthenospheric to deep lithospheric mantle sources.

Further evidence that the orogenic-like magmatism in the IVZ predates the alkaline anorogenic magmatism is provided by some dykes which show both orogenic-like and anorogenic affinities. Amphibole in the central part of dykes belonging to this group is enriched in HFSE and grades to HFSE-poor composition towards the margins, suggesting that an HFSE-poor dyke was intruded and overprinted by HFSE-rich melt(s).

The results of this study confirm a geochemical change of the Triassic-Early Jurassic magmatism of the IVZ from orogenic-like magmatism, typical of post-collisional settings, to anorogenic alkaline magmatism, common in intraplate to extensional settings, and places a temporal correlation of Early Mesozoic magmatism in the IVZ to those in the eastern and central sectors of the Southern Alps (see Ogunyale et al., 2024a; Bonazzi et al., 2024).

Shoshonitic orogenic-like magmatism in the Dolomites and correlation to IVZ magmatism

The new collection of basaltic lavas and dykes from the Dolomites (eastern Southern Alps) show shoshonitic orogenic-like affinity characterized by depleted HFSE (Nb-Ta-Ti), and enriched Pb, LILE and LREE compositions coupled with enriched “crust-like” Sr-Nd isotopes, typical of Middle Triassic magmatism in the area (Fig. 3b). Combined with whole-rock Hf (first-ever dataset) and Pb isotopes, the composition of the studied lavas and dykes indicate a close similarity to the IVZ HFSE-poor dykes with “orogenic-like” affinity. The new Hf ($\epsilon\text{Hf}_{(t)}$: +3.8 to -2.8) and Pb (EM-II like) isotopic composition of the Dolomitic lavas and dykes, in combination with the geochemical composition of the IVZ HFSE-poor dykes further support the derivation of the Southern Alps Middle Triassic orogenic-like magmatism from heterogeneous, metasomatized lithospheric mantle sources containing large amounts of recycled continental (and possibly oceanic) crust materials. Interrelation between whole-rock trace elements and isotopic ratios further confirms

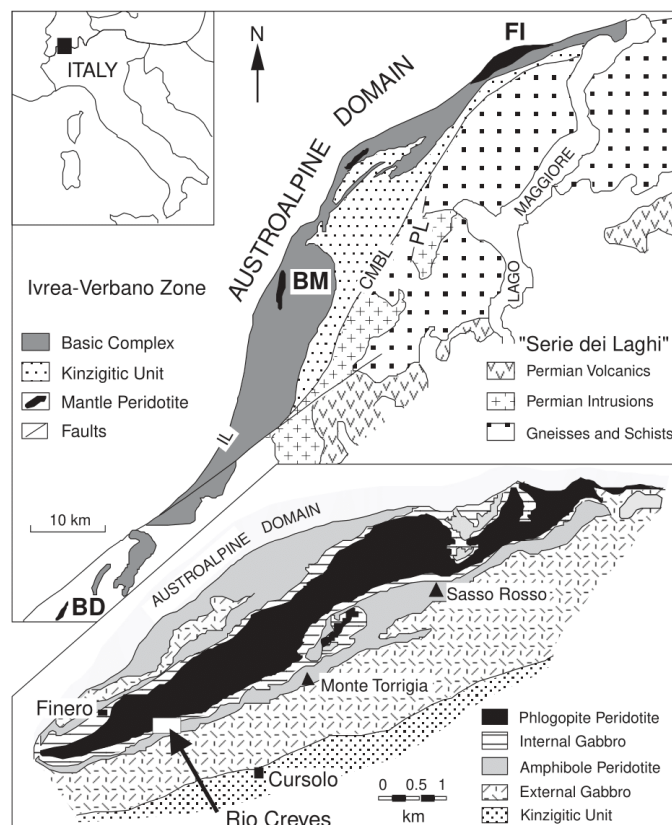


Figure 2 Geological maps of the **a)** Ivrea-Verbania Zone and **b)** the Finero Complex (indicated as FI in **a)** where the studied dykes and phlogopite-peridotite massif were sampled. The location of the three Iherzolitic massifs at Premosello, Balmuccia (BM) and Baldissero (BD) are indicated in **(a)**. IL - Insubric Line, PL - Pogallo Line, CMBL - Cossato-Mergozzo-Brissago Line (Zanetti et al., 1999).

the limited role of post-melting crustal contamination processes in the evolution of the Southern Alps orogenic-like magmatism.

To reconcile the geochemical and isotopic signatures of the Southern Alps Triassic-Early Jurassic magmatisms with geodynamic aspects, we proposed a model in which the magmatisms were triggered by the Paleotethys subduction but the recycled continental crust materials in the mantle sources of these magmatisms are related to crustal materials brought down to mantle depths by the Variscan and/or older subduction events, as well as by the delamination of the roots of the Variscan chain (see Ogunyale et al., 2024a).

Continental crust recycling in the upper mantle beneath the Southern Alps and relation to Triassic magmatism: Evidence from the Finero Phlogopite Peridotite

The detailed petrological, geochemical and isotopic study of Triassic-Early Jurassic magmatic and volcanic rocks from the Southern Alps have provided evidence for the occurrence of the heterogeneous continental crust-contaminated mantle beneath the region. To provide further evidence for the recycling of continental crust materials in the subcontinental lithospheric mantle (SCLM) beneath the Southern Alps and relate this

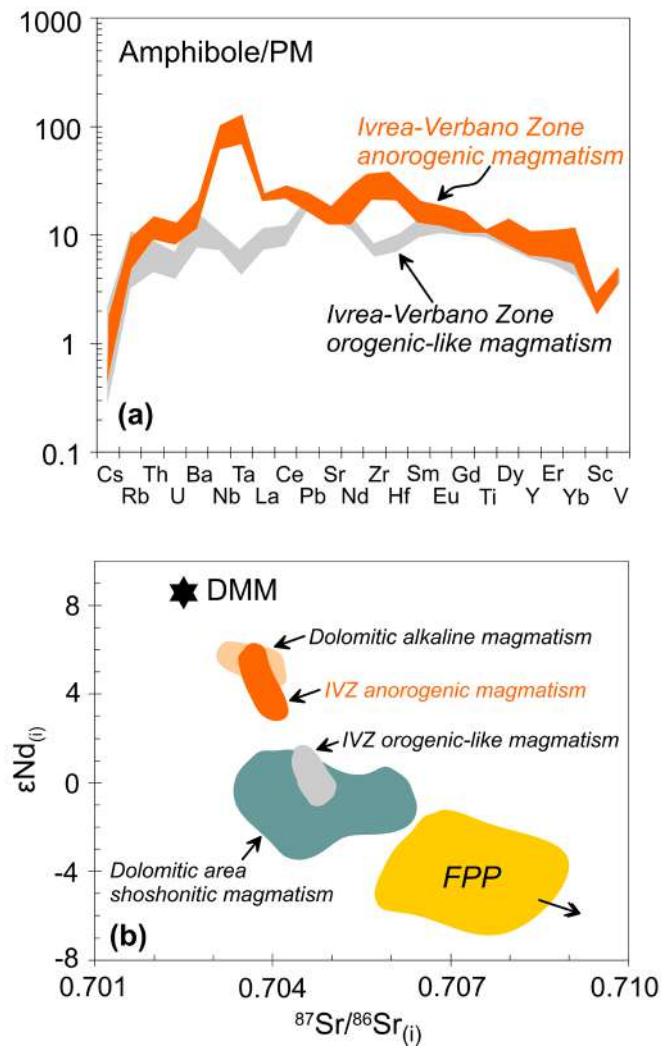


Figure 3 a) PM-normalized incompatible trace elements compositions of amphiboles from Triassic orogenic-like and anorogenic magmatic rocks from Finero, Ivrea-Verbano Zone. b) $\epsilon\text{Nd}_{(i)}$ and $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ composition of the IVZ and Dolomitic Triassic orogenic-like and anorogenic magmatisms. The composition of the Finero Phlogopite Peridotite (FPP, 300 Ma) and Depleted MORB Mantle (DMM, 200 Ma) are also plotted. Plotted data are from this study and literature (Voshage et al., 1987; Stähle et al., 2001; Casetta et al., 2019, 2021; Lustrino et al., 2019; De Min et al., 2020; Giovanardi et al., 2020).

mantle composition to the Triassic magmatic events, the orogenic mantle massifs exposed in the IVZ are important. The Finero Phlogopite Peridotite (FPP) which hosts abundant Triassic-Early Jurassic dyke swarms is particularly relevant in this investigation, as the FPP based on mineralogical and trace element characters could represent, at least, a close analogue of the mantle sources of the Southern Alps Middle Triassic orogenic-like magmatism (Casetta et al., 2021; Ogunyele et al., 2024a).

The FPP is a pervasively metasomatized orogenic peridotite massif in northern IVZ formed by well-equilibrated phlogopite- and amphibole-bearing harzburgites, dunites and pyroxenites (websterites and orthopyroxenites). Bulk-rock peridotite composition is characterized by large MgO contents. Accordingly, all mineral phases from the peridotite exhibit a depleted geochemical character, such as high Mg# (in all the silicates) and Cr# (in all silicates and spinel), being geochemically similar to the highly depleted peridotites formed in supra-

subduction zones. Despite the depletion in incompatible elements, the clinopyroxene from the peridotite and websterite show selective enrichments in LILE and LREE, and strong fractionation in the L- versus M-HREE. Similarly, amphiboles are also enriched in LILE, LREE and Pb, and strongly depleted in HFSE (Nb, Ta, Zr, Hf, and Ti). In terms of radiogenic isotope composition, amphiboles from the peridotite and websterite are characterized by high $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$ with $\Delta 8/4$ and $\Delta 7/4$ ranging from 61.6–64.5 and 12.3–14.9, respectively. This elevated Pb isotopic signature is coupled with radiogenic $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ (0.706746–0.707632), and unradiogenic $\epsilon\text{Nd}_{(i)}$ (–1.9 to –3.2) and $\epsilon\text{Hf}_{(i)}$ (+0.1 to –1.9) (Fig. 3b). As a whole, the geochemical and isotopic signatures of the Finero phlogopite peridotite suggest that the upper mantle was metasomatized by hydrous silica-saturated melts with a geochemical affinity similar to that of the continental crust. We thereby propose that these metasomatizing melts were largely derived from the partial melting of continental crust subducted and/or delaminated into the upper mantle during the Variscan orogenic cycle (i.e., Pangea amalgamation), an event likely occurring in the Upper Carboniferous to Lower Permian times. We conclude that the event of recycling of continental crust and metasomatism within the upper mantle, as testified by the Finero peridotite, represents a deep expression of the mantle-derived magmatism with continental crust components documented in the IVZ and widespread in the other sectors of the Southern Alps until the Late Triassic-Early Jurassic.

Time of accretion of IVZ Iherzolites and geodynamic evolution of Adriatic Plate

Orogenic Iherzolite massifs outcropping at Premosello, Balmuccia and Baldissero in central to southern IVZ represent unique fragments of the subcontinental lithospheric mantle (SCLM) underlying the Southern Alps (in Adriatic Plate) which were tectonically exhumed to crustal levels, probably since the end of the Variscan orogeny (e.g., Decarlis et al., 2023). New mineral chemical and Nd isotopic data coupled with the first-ever Hf isotopic data on Sp-Iherzolite and pyroxenite samples from these massifs place fundamental constraints on the timing, mechanism and geodynamic environment of accretion of the IVZ Iherzolithic mantle to the Adriatic SCLM.

Major and trace elements composition of mineral phases (Ol, Opx, Cpx, Sp) from the IVZ Iherzolites indicate that they range from residual to melt-reacted peridotites, and are similar to abyssal peridotites. Geochemical modelling of REE patterns of Cpx suggests that the Balmuccia and Baldissero peridotites experienced ~5% fractional melting of a DM-like source, whereas Premosello peridotite recorded relatively higher fractional

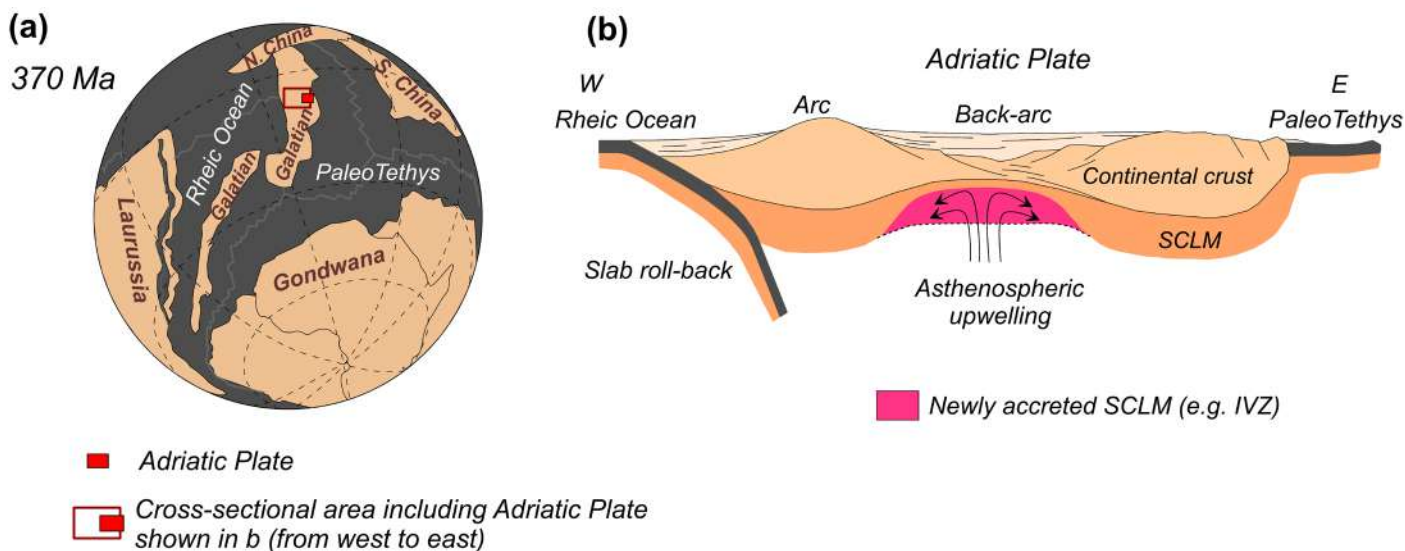


Figure 4 a) Global reconstruction of the Devonian showing the location of the Adriatic Plate within the Galatian terrane (modified after von Raumer et al., 2013). b) Schematic model of accretion of the IVZ Iherzolitic SCLM by asthenospheric upwelling in the Devonian (adapted from Siegesmund et al., 2021).

melting (~10-12%). All Iherzolite samples, except for a few from Balmuccia and Baldissero, show slight enrichment in LREE indicative of metasomatic enrichment during and/or after partial melting. The present-day Nd-Hf isotopic compositions of Cpx further confirm the difference between the three peridotite bodies. Cpx samples from the three mantle massifs display large variations in present-day $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratios, with Balmuccia and Baldissero samples plotting along the mantle Nd-Hf isotope array and the Premosello samples plotting above the array. Taken as a whole, the three mantle massifs preserve well-defined correlations between present-day Nd-Hf isotope ratios and parent-daughter ratios, which yielded errorchrons of 370 Ma, with an uncertainty of ± 20 Ma, exceptionally consistent for both Sm-Nd and Lu-Hf systematics. This age is also consistent with Sm-Nd pseudo-isochrons (378 ± 48 Ma, 390 Ma; Obermiller et al, 1992; Obermiller, 1994) and peak Paleozoic Re depletion ages (350-500 Ma; Mazzucchelli et al., 2010; Wang et al., 2013) previously reported for the Balmuccia and Baldissero Iherzolites.

Although the Balmuccia and Baldissero Iherzolites show peak Paleozoic Re depletion ages (T_{RD}), these massifs also preserve a few Proterozoic depletion ages (up to 1.6 Ga). These Proterozoic ages could imply that the IVZ Iherzolitic mantle is an ancient depleted (i.e., cratonic) mantle that was metasomatised (or re-fertilized) around 370 Ma. If this was the case, however, the samples might not have preserved similar errorchrons in both Nd and Hf systematics. Moreso, when the Nd-Hf isotopic composition of all Iherzolite Cpx samples from the three studied massifs are corrected to 370 Ma, highly radiogenic signatures ascribable to any significant melting event in the Proterozoic were not found. Rather, Premosello peridotites exhibit initial Nd-Hf isotopes ($\epsilon\text{Nd}_{(i)} = +4.3$ to $+6.4$, $\epsilon\text{Hf}_{(i)} = +2.3$ to $+7.1$) similar to Balmuccia and Baldissero

peridotites ($\epsilon\text{Nd}_{(i)} = +2.9$ to $+5.8$, $\epsilon\text{Hf}_{(i)} = +5.5$ to $+16.4$) suggesting that prior to ca. 370 Ma, the three peridotite bodies had similar isotopic and geochemical compositions. The few unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotopes which yielded Proterozoic Re depletion ages in the IVZ Iherzolites may, therefore, be interpreted as the composition of ancient mantle lithosphere relics delaminated and entrapped in an upwelling asthenosphere. Hence, rather than portions of an ancient depleted (cratonic) SCLM refertilized in more 'recent' times, we prefer the possibility that the three peridotite bodies were in the asthenospheric mantle and evolved with a similar geochemical composition until ca. 370 Ma.

Supported by isotopic and trace elements modeling, it is hypothesized that at ca. 370 Ma, an intrinsically homogenous asthenospheric mantle section suffered variable degrees of partial melting (i.e., up to 12% in Premosello, ~5% in Balmuccia and Baldissero) plus different extents of nearly contemporaneous refertilization which partly obscured the depletion signatures. It is therefore argued that the two errorchrons pointing to ca. 370 Ma may represent the age of depletion for both the residual and refertilized peridotites, also coinciding with the timing of the metasomatic event for the refertilized rocks.

In light of the Nd-Hf isotopic evidence herein presented combined with previously reported Sm-Nd pseudo-isochrons and peak Paleozoic Re depletion ages, we constrain the accretion of the Iherzolitic SCLM beneath the IVZ to the Upper Devonian (i.e., 370 ± 20 Ma). At that time, the Adriatic Plate was part of the Galatian terrane (Fig. 4a), a continental ribbon detached from Gondwana and accreted to the margin of Laurussia shortly before the Late Carboniferous Variscan collision (von Raumer et al., 2013). At ca. 370 Ma, the northern and western borders of the Galatian terrane were characterized by a long-lasting extension in a back-arc region caused by

the subduction of the Rheic Ocean, whereas the southern and eastern ones were passive margins of the Paleotethys. The lithospheric thinning led to the development of large basins associated with intrabasinal magmatism, starting from ca. 370 Ma and well documented in both Southern Alps and Austroalpine units (Siegesmund et al., 2021). In this framework, we propose that the IVZ Iherzolitic massifs were accreted to the Adriatic SCLM through asthenospheric upwelling triggered by Variscan intra-continental extension in a back-arc setting related to the subduction of the Rheic Ocean (Fig. 4b). Hence, rather than the product of recent processes of rejuvenation of old cratonic roots, we here suggest formation of the IVZ Iherzolitic SCLM in "recent" continental back-arc settings, where a combination of low-degree melting and nearly contemporaneous melt migration produce fertile mantle lithologies (see Ogunyele et al., 2024b).

CONCLUSION

This thesis unravels the complex tectono-magmatic evolution of the Southern Alps during the Triassic with a special focus on the westernmost (IVZ) and eastern (Dolomites) sectors of the region. A multidisciplinary approach including detailed field observation, petrography, mineral chemistry, U-Pb zircon geochronology, isotope geochemistry and geochemical modeling was applied to suites of Triassic to Early Jurassic magmatic and volcanic rocks outcropping in the Southern Alps. Additional constraints were provided from Iherzolitic to harzburgitic mantle massifs outcropping in the IVZ. The detailed petrological, geochemical and geochronological studies in the Southern Alps document a shift of the Triassic magmatism from orogenic-like to anorogenic alkaline affinity throughout the region. This geochemical shift is related to a change in the mantle sources of these contrasting magmatisms from a metasomatized lithospheric mantle containing a significant amount of recycled continental crust components (similar to Finero phlogopite peridotite) to variably depleted asthenospheric sources. A revised geodynamic model is proposed whereby the magmatisms were triggered by the Paleotethys subduction but the recycled continental crust materials in the mantle sources of these magmatisms are related to crustal materials brought down to mantle depths by the Variscan and/or older subduction events, as well as by delamination of the roots of the Variscan chain. The recycling of continental crust materials in the mantle beneath the Southern Alps is further testified to by the Finero peridotite.

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Evaluation of Thermal Potential of the Amiata geothermal field: Geochemical, Petrologic and Petrophysics data

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INTRODUCTION & AIM

Monte Amiata is a hybrid volcano outpoured between 305 and 231 ka (Laurenzi et al., 2015) during the middle-Pleistocene. Their products consist of a succession of lavas and domes, with composition from trachyte/trachydacite to olivine-latite (Conticelli et al., 2015a; Ferrari et al., 1996; Marroni et al., 2015). The volcanic edifice was built during magma emission from an eruptive fissure aligned along the NNE-SSW direction (Brogi, 2008). The eruptive activity took place in two-short lived episodes (Conticelli et al., 2015a; Ferrari et al., 1996; Marroni et al., 2015), seemingly separated from a level characterised by a strong weathering alteration (e.g., Certini et al., 2006; Principe & Vezzoli, 2021). Key characteristics of lavas and domes encompass abundant rounded magmatic enclaves (Ferrari et al., 1996 and references therein), flat or rounded crustal meta-sedimentary xenoliths (van Bergen, 1983), and the prevalence of sanidine megacrysts (Balducci & Leoni, 1982) within. The area around the volcano underwent a regional uplift of about 2 km, extending from Monte Amiata to Radicofani volcanoes, covering an area of 35 x 50 km caused by an unspecified magma intrusion at a depth of 5-7 km (Acocella & Mulugeta, 2001; Acocella et al., 2002). Geological (van Bergen, 1983; Bigazzi et al., 1981; Calamai, 1970; Mazzuoli & Pratesi, 1963), hydrogeochemical (Magi et al., 2019; Minissale et al., 1995), geochemistry of gasses (Fron dini et al., 2009a; Nisi et al., 2014; Sbrana et al., 2020; Vaselli et al., 2013), and geophysical (Girolami et al., 2017; Volpi et al., 2003) studies revealed two significant geothermal reservoirs with high temperatures (> 250°C) and a marked ground CO₂-flux (Fron dini et al., 2009b; Sbrana et al., 2021). Despite extensive research, debates persist regarding the stratigraphic relationships among lava flows and domes, the petrogenesis of silicic end-member magma, the magmatic chamber architecture, the petrophysics characteristic of xenoliths and the thermo-chemical interaction with magma. The main objective of this study is to evaluate the thermal energy emitted by the magmatic source and how this propagates

into the metamorphic basement as a function of the host country-rock type. Several objectives were achieved, such as the stratigraphic relationship among lavas and domes, the characterisation of the mineral chemistry of crystals from igneous and meta-sedimentary rocks, the investigation of the volatile phase nature trapped by melt inclusions, the determination of a Temperature and Pressure range referred to the magmatic reservoir at the eruption moment, the quantification of the water content, the Fe-redox conditions of brown mica from magmatic rocks and meta-sedimentary xenoliths, and the development of a model outlining the architecture and the evolution of the magmatic reservoir.

This study employs a multidisciplinary approach encompassing a new stratigraphy of volcanic rocks, petrographic investigations, whole-rocks geochemistry, mineral chemistry and isotope chemistry analyses, X-ray diffraction and crystal chemistry of brown micas, microthermometry experiments on melt inclusions and thermobarometry calculations; also, seismic wave velocities propagations and thermal conductivity of basement rocks.

RESULTS & DISCUSSION

A new stratigraphy of volcanic rocks

This study reports a new and original stratigraphy of the Monte Amiata volcano. The new stratigraphic sequence follows the guidelines issued directly by ISPRA according to "Quaderni del Servizio Geologico D'Italia" (Quaderni serie III, vol. 12, fascicolo III, aggiornamento al quaderno n.1/1992).

The "Bagnore" synthem (**BGE**) (Fig. 1a) represents the stacking of multiple viscous lava flows all around the volcano, characterised by a flat morphology and the typical sin-depositional structure (i.e., shear zone) in which are hosted major crustal meta-sedimentary xenoliths and minor rounded magmatic enclaves (van Bergen, 1984; Conticelli et al., 2015a). Rocks are porphyritic with major sanidine, brown mica, zoned plagioclase, ortho- and

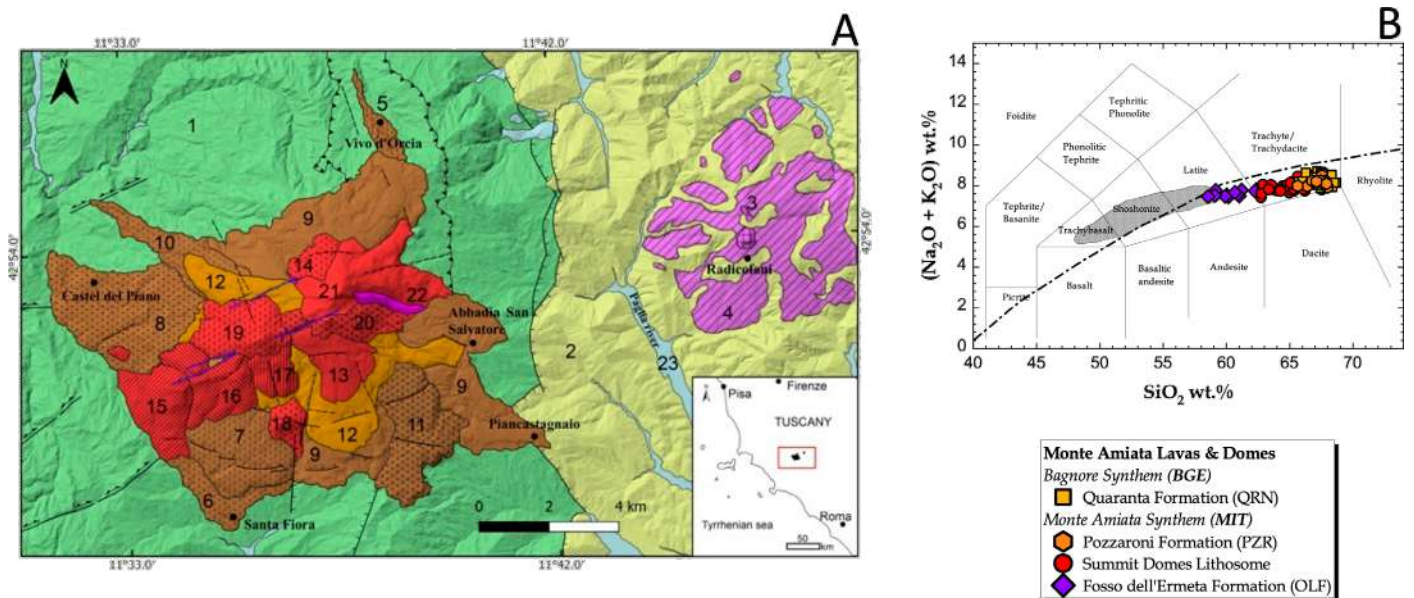


Figure 1 a) Geographic location and Geological chart of the Monte Amiata–Radicofani volcanic area (courtesy of Sepulveda-Birke J.P.); BGE (5, 6, 7, 8, 9, 10, 11), PZR (12), MIT (13, 14, 15, 16, 17, 18, 19, 20, 21), OLF (22). b) Total Alkali vs. Silica classification diagram of volcanic rocks from Monte Amiata, the grey field represent data of magmatic enclaves from Conticelli et al. 2015a.

minor clinopyroxenes, set in a glassy groundmass with frequent occurrence of sanidine fragments. The “Monte Amiata” synthem (MIT) (Fig. 1a) represent the summit domes starting from the “Pozzaroni” formation (PZR) and moving toward the East direction along the eruptive fissure. Rocks are porphyritic microcrystalline with major sanidine megacrystals, and phenocrysts of zoned plagioclase, clino- and ortho-pyroxenes, brown mica, all immersed in a groundmass made up of nanolites of plagioclase, pyroxenes, ±olivine and glass. The “Fosso dell’Ermata” formation (OLF) is represented by two small lava flows located on the Eastern flank of the volcano and is already part of the MIT, testify the closure moment of the eruption. OLF rocks are porphyritic with microcrysts of zoned plagioclase, brown mica, clino- and ortho-pyroxenes, set in a groundmass of the same phases plus olivine. In the MIT lavas and domes, the magmatic enclaves increase the size and the mafic composition, while meta-sedimentary xenoliths are less common.

Petrology and Geochemistry

Whole-rocks geochemistry investigations of the volcanic rocks indicate a wide compositional spread passing from trachydacite to latite (Fig. 1b), whereas trace elements indicate the important role played by sediments during the subduction suggesting a primary recycling of a sedimentary component within the upper mantle (Conticelli & Peccerillo, 1992; Avanzinelli et al., 2008; Conticelli et al., 2015b).

Isotope chemistry reveals a similar isotopic composition for the different lava tongues of (BGE) ($^{87}\text{Sr}/^{86}\text{Sr} = 0.713019$) all around the volcano, which begins to change from the “Pozzaroni” formation (PZR) (0.71301–0.71292) and continues to vary in the Sr-ratio towards

the summit domes (MIT) (0.712905) and the final lavas (OLF) (0.71161). The “Pozzaroni” formation was placed temporally and spatially between the basal complex (i.e., “Bagnore” synthem) and summit domes (i.e., “Monte Amiata” synthem), representing an intermediate outcrop with similar features between BGE and MIT rocks (Fig. 1a).

The whole-rock geochemistry of thermo-metamorphic xenoliths indicates a generic SiO_2 - and Al_2O_3 -rich rock typical of a pelite, with enrichment in barium and strontium. Isotope chemistry reveals an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71675.

Mineral Chemistry

Mineral chemistry investigations are carried out on plagioclase, sanidine, brown mica, clino- and orthopyroxenes, and glass from groundmass and melt inclusions (MIs). In particular, brown micas from igneous and meta-sedimentary suites exhibited different geochemical signatures suggesting distinct growth environments that slightly interact with each other (Fig. 2a), followed similarly by the geochemical signature of sanidine; clinopyroxenes record a transition from sub-alkaline to alkaline affinity of his hosted rocks (Fig. 2b). μSr -Isotope investigation on sanidine megacrysts indicate a high-radiogenic core (0.71338) and a less-radiogenic rim (0.71305) (Fig. 2c) suggesting a strong disequilibrium condition during the growth and the nucleation set in a complex magmatic environment and starting from an ancient sub-crustal mantle-derived magma, which gradually begins to undergo a magma mixing with a more mafic and less radiogenic magma. Also, brown mica, plagioclase and sanidine record the presence of peraluminous component released from magmatic fluids during a near-soli-

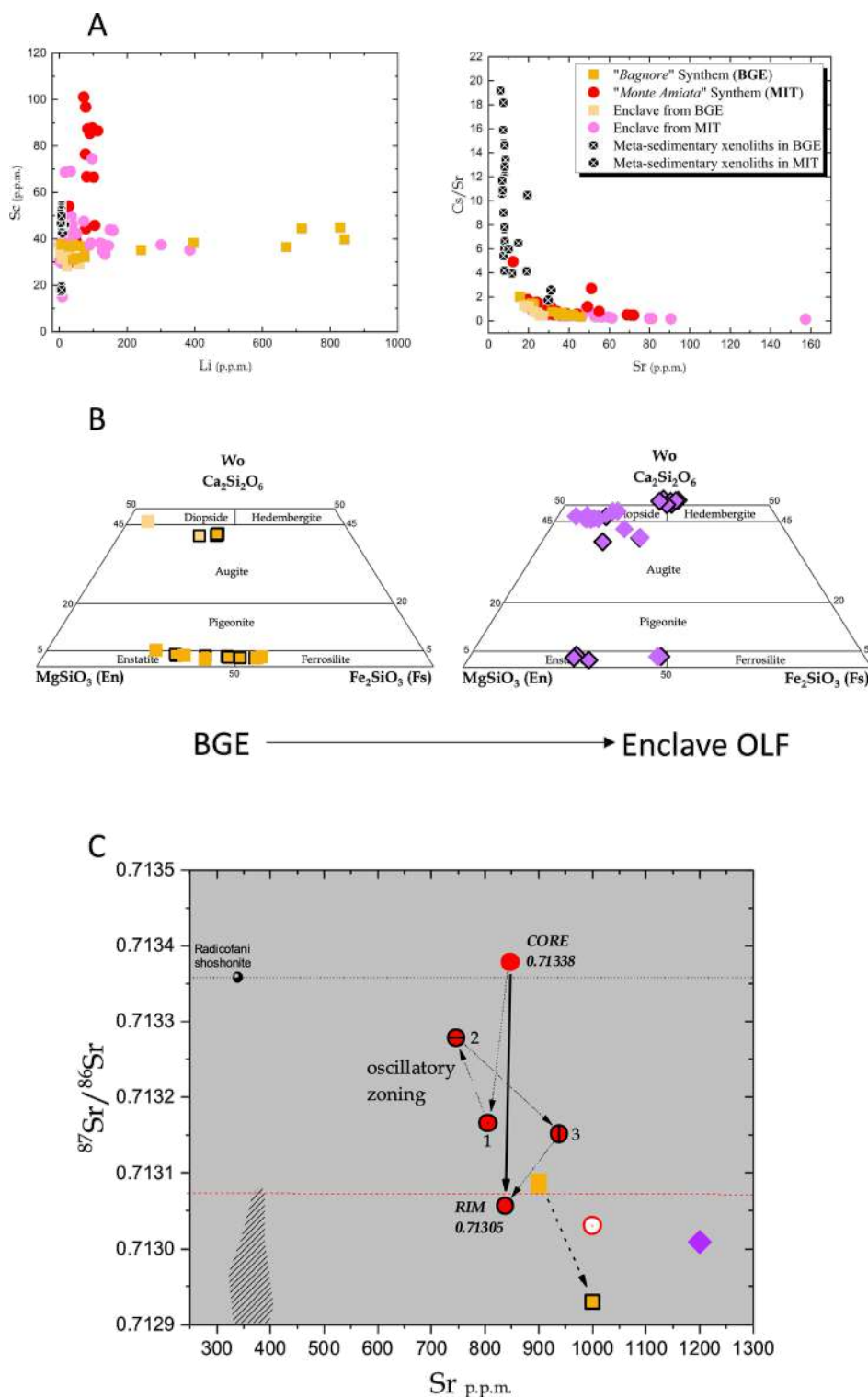


Figure 2 a) Brown Micas trace-elements chemistry denotes an enrichment in lithium for samples from BGE while an enrichment in scandium for crystals from MIT (left graph); it also suggests a mutual interaction between magma and crustal xenolith (right graph). **b)** Clinopyroxene major-elements chemistry from BGE (left) and OLF magmatic enclaves (right) rocks suggesting a change in the magmatic affinity passing from sub-alkaline to alkaline. **c)** μSr -isotope chemistry of sanidine megacrysts exhibits characteristic oscillatory zoning and suggests a combination of fractional crystallisation plus magma mixing processes, revealing the chaotic nature of the system.

condition, suggesting by: *i)* the partial melting of xenoliths associated with a release of Rb, Al, and Fe-rich peraluminous melts, and *ii)* the signature in lithium is interpreted as an indicator that characterises the marginal zone of the magmatic chamber, where the crystallisation is pushed toward the limit of the melt-impregnated regime condition (i.e., < 20 - 50 vol.% of melt; Koyaguchi & Kaneko, 2000). Textural and mineral chemistry evidence supports the process of continuous fractional crystallization followed by numerous injections of hot and mafic magmas. Also, there is compelling information about an active interaction between magmas and meta-sedimentary xenoliths indicated by mineral reactions and compositional signatures and by the circulation of hy-

drothermal-magmatic fluids in the marginal shell zone of the magmatic chamber. Such isotopic disequilibrium within individual sanidine megacryst samples provides compelling evidence of dynamic magma interactions in a chaotic environment, highlighting the potential coexistence of distinct magma sources, or stages, within the magmatic system. This suggests a possible co-genetic relationship between the trachytic magma (HKCA) of Monte Amiata (Conticelli et al., 2015a) and a common mantle source component with the nearby Radicofani volcano (Conticelli et al., 2011).

Thermobarometry calculations

Different thermobarometric methods, as machine learning and traditional calculation, are applied using the chemistry investigations carried out on plagioclase, clinopyroxene and glass. In particular, the automatised calculations are made by Thermobar (Wieser et al., 2022) and GAIA (Chicchi et al., 2023), with the capability of being able to use a wide range of thermodynamic equations from experimental literature (e.g., Putirka et al., 2003; Putirka, 2008; Waters & Lange, 2015; and references therein). Temperature, pressure and water content investigated reveal a volcanic condition represented by a shallow hypabyssal magmatic reservoir with deep mafic roots, characterised by a T - P - $X_{\text{H}_2\text{O}}$ range of 900 - 1160°C, 1 - 9 kbar, and H_2O wt.% between 0.8 - 2.1, respectively (Fig. 3a-b).

Melt inclusions microthermometry constrain

Two types of MIs are present within sanidine mega- and phenocrysts: *i*) a *euhedral* type, ranging in size from 200 to 25 μm , displaying a regular geometry of rooms. The colour of glass ranges from brown to colourless, from nanocrystalline to glassy matrix. Bubbles are present in large and small specimens, appearing mostly black in transmitted light, occupying $\frac{1}{2}$ and $\frac{1}{4}$ of the total volume of the MI. *ii*) An *anhedral* type frequently show a size up to 200 μm , the colour of the glass ranging from brown to colourless and the bubble is large and accompanies the irregular shape of the MIs. Microthermometric experiments are held on MIs extracted from megacrysts core and rim zone, in which no differences in temperature are recorded between them. According to the guidelines of Frezzotti (2001), results of heating experiments reveal an observed average T_1 of 994°C, and an average T_2 of 1114°C, while T_3 is never reached. During the increase in temperature, the bubble is never reabsorbed by the melt.

CO₂-dominated plumbing system

Raman spectroscopy investigations are conducted on the bubble of heated MIs. Analyses reveal the presence of pure CO_2 showing the typical peaks at 1387.05 cm^{-1} and 1283.67 cm^{-1} with a constant Fermi diad (Fermi, 1932) of 103.4 cm^{-1} . The amount of carbon dioxide observed within sanidine MIs aligns with the low water content measured indirectly by plagioclase-liquid hygrometer (Waters & Lange, 2015) and by the crystal-chemistry investigation on brown mica.

Magma-Crust interaction

The degree of interaction between the magmatic intru-

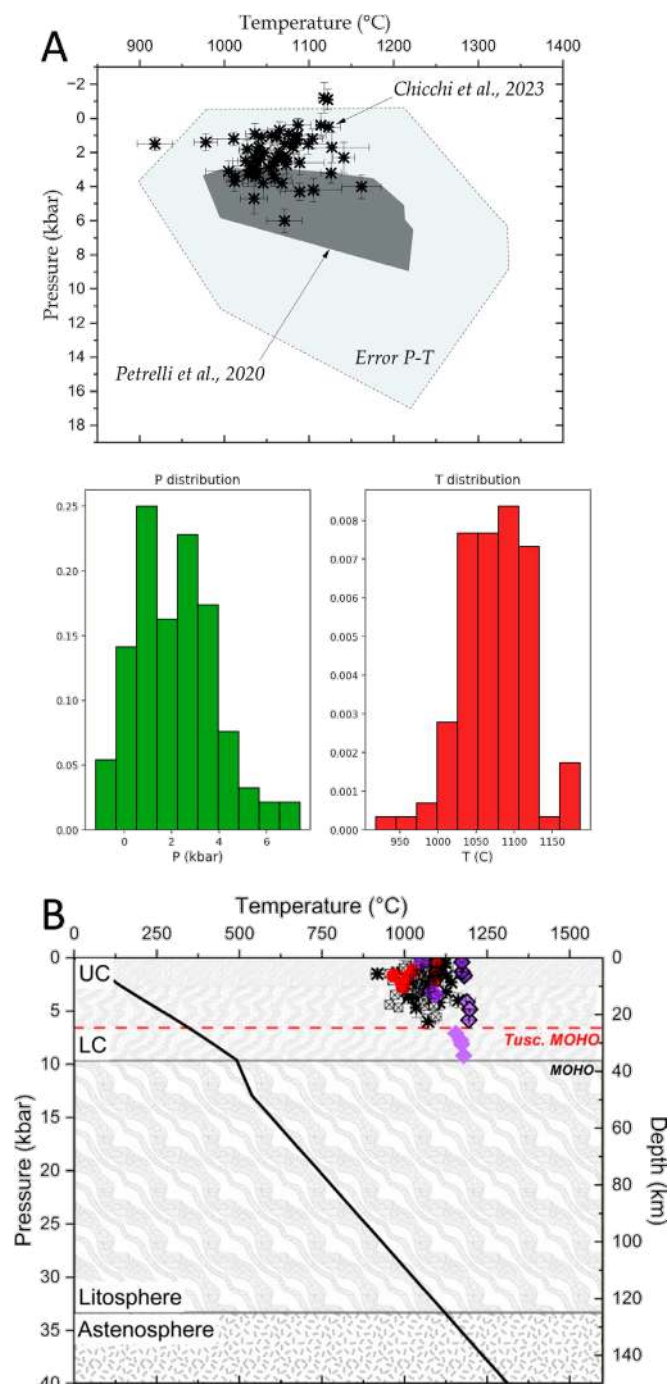


Figure 3 a) Pressure and Temperature space calculated by Machine Learning. b) Schematic representation of the magmatic intrusion in an ideally reconstructed lithospheric mantle structure.

sion and the metamorphic basement can be understood using the crustal meta-sedimentary rocks that could be found in lavas and domes as xenoliths. A detailed study on petrography, geochemistry, seismic wave velocity propagation and thermal propagation of crustal xenoliths is mandatory to understand how the heat is released from the magmatic intrusion through the metamorphic rock basement. Meta-sedimentary rocks show a wide spectrum of facies and textures typically of contact metamorphosed pelites passing from *slate* (500-570°C; Fig. 4a), *semi-hornfels* (600-650°C; Fig. 4b) to *hornfels* (700-750°C; Fig. 4c-d), changing progressively the mineralogic assemblage. The observed transition indicates an increase in temperature, which may represent the thermo-metamorphic shell surrounding the magma cham-

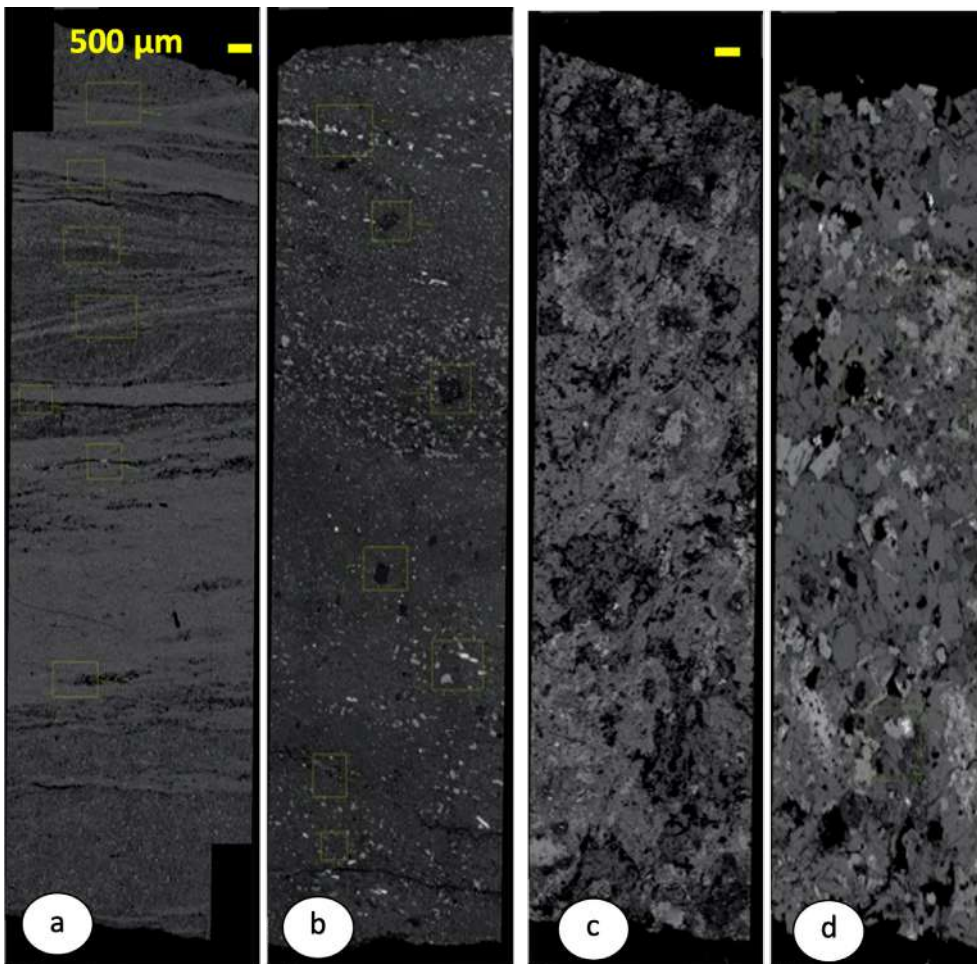


Figure 4 SEM-BSE image of crustal meta-sedimentary xenoliths hosted by lavas and domes. Following the fabric and mineral features of xenoliths, it is possible to recognise an order related to the thermo-metamorphism of pelitic rocks, sketchily representing the contact aureole around the magmatic reservoir. The recognised facies are a) slate; b) semi-hornfels; c-d) hornfels.

ber, also known as the contact aureole. The progressive change in their mineral fabric denotes variations in the petrophysics proprieties, such as the V_p/V_s ratio and the thermal conductivity/diffusivity. Using all information, from thermobarometry, geochemistry and petrophysics, is possible to quantify the thermal propagation between the magmatic body and the surrounding crustal country rocks.

The geothermal potential calculation

The search for geothermal energy in the Monte Amiata area began in the 1950s (Barelli et al., 2010; Bertini et al., 1995), and together with the active Larderello geothermal field (Parri & Lazzeri, 2016 and references therein), it constitutes a strategic national and regional energy hub. The work carried out in this study attempts to go beyond the classic approach of studying a geothermal field but attempts to theorize a very-deep reservoir within Tuscany basement rocks, and beneath the Monte Amiata area, integrating all the information derived from investigations of crustal and volcanic material. Theoretically, it is possible to create multiple synthetic reservoirs through the application of Hot Dry Rock (HDR) technology (Rummel, 2005; U.S. Department of Energy, 1997), bypassing the shallow (Barelli et al., 2010) and the deepest (Bertini et al., 1995) geothermal reservoirs currently used for the energetic production. The calculation was made

bypassing all problems related with the engineering application of HDR technology in a complex geothermal field such as Monte Amiata. The present-day thermal emission from the magmatic heat source is characterised by a temperature of 820°C (i.e., calculated using a ratio of 100°C/100 ka; González et al., 2022; Zambra et al., 2022), quantifiable by 10^{24} calories emitted per km^3 . Considering the possibility of being able to create and exploited, by means of high-pressure fluids, a reservoir of fractured rocks at a depth of about 5 km and with a volume of 10 km^3 with a maximum theoretical energy production of 3277 MW/year or 0.33 GW_{yt} .

CONCLUSIONS

Results of stratigraphy, petrography, geo- and mineral-chemistry, and isotope chemistry suggest a single extrusive eruption involved in the setting of lavas and domes. The petrogenesis of high-silica magmas could be explained by an intrusion of sub-crustal mantle-derived HKCA/SO magmas (i.e., Tuscany-type; Conticelli et al., 2010; Peccerillo, 2017) in the lithospheric crust, which undergoes a process of R_xMFC due to the progressive injection of a hot and mafic silica-undersaturated potassic mantle-derived magma (i.e., Roman-type; Conticelli et al., 2010; Peccerillo, 2017) (Fig. 5a-b). The geochemical model performed on the groundmass glasses of trachydacitic rocks and the mineral chemistry investigations supports the presence of a micro-assimi-

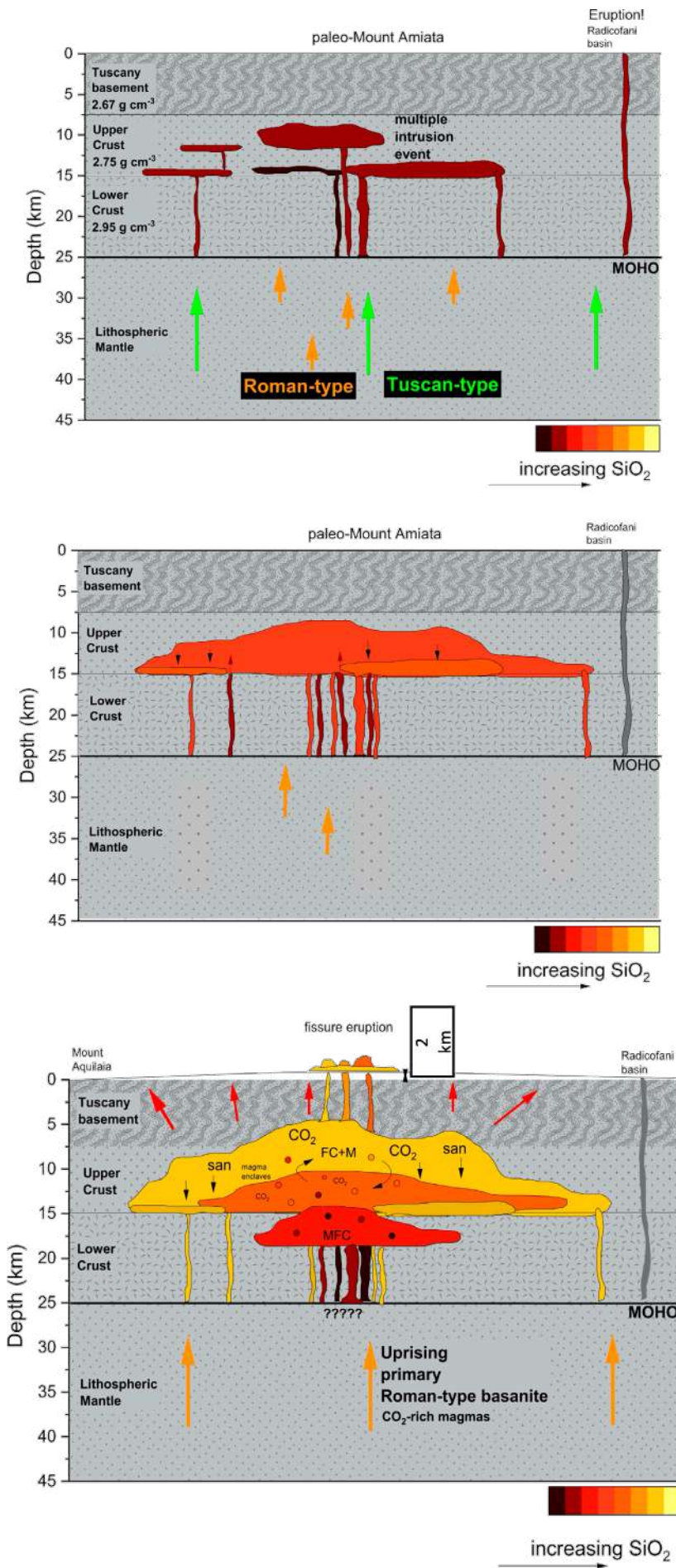


Figure 5 Reconstruction of the magmatic intrusion beneath the studied area. **a)** The eruption event of Radicofani volcano signing the moment of the first intrusion of HKCA/SHO mantle-derived magmas (i.e., 1.2 Ma). **b)** The continuous Fractional Crystallisation process plus a magma mixing with Roman-type mantle-derived magmas involves the evolution and the increase in size of the magmatic reservoir. **c)** In the last stage, prior to the eruption of Monte Amiata volcano (i.e., 0.30 - 0.23 Ma), the magmatic reservoir was characterised by a zoned magmatic chamber with different levels, a mafic magma roots in depth and a differentiated magmas on the top.

lation process of peraluminous melts/fluids release from pelitic xenoliths, undergoing pyrometamorphic processes during the last stage of the magmatic differentiation. The application of geothermobarometers revealed a

volcanic temperature range from 900 to 1160°C, with a largely variable storage pressure between 0.1 and 0.9 GPa. Microthermometry experiments on sanidine melt inclusions confirm these volcanic temperatures in the

range between 900 and 1075°C. The Pressure and Temperature found suggest volcanic conditions during the eruption event, supporting the idea of mantle-derived magmas and a storage depth from ≈ 3 to ≈ 20 km (Fig. 5c). The large amount of CO₂ indicates mantle processes as the main players, furthermore, influencing the amount of water dissolved in magma and, additionally, opens the way on the potential release of carbon-rich fluids from thermo-metamorphosed crustal xenoliths directly into the magmatic reservoir. The architecture of the magma chamber of Monte Amiata volcano can be idealised with a batholith-shape divided into two zones with different thermo-chemical features, characterised by a differentiated rock in the most marginal inner zone of the magmatic reservoir and a contact aureole in the outer zone, and mafic roots deep down (Fig. 5c). The calculated present-day temperature emitted by the heat source is about 820°C, quantifiable by 10²⁴ calories emitted per km³, and a maximum theoretical energy production of 3277 MW/year or 0.33 GW_{yt}.

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Architecture and construction mechanisms of post-collisional granitoid complexes: an integrated field, microstructural, AMS and EBSD study of the late Variscan Serre Batholith (southern Calabria)

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INTRODUCTION

This work aims to better understand the architecture and construction mechanisms of granitoid batholiths in post-collisional settings, also investigating the relationships between regional tectonics, magma emplacement, and structural evolution of the granitoid bodies from supra- to low-temperature subsolidus conditions.

In this respect, the late Variscan Serre Batholith in southern Italy is an ideal case study because, despite its limited extension (c. 1200 km²), it is a ca. 13 km-thick composite and zoned batholith, which is exposed with continuity from floor to roof (Fig. 1a, b). Basal tonalites and quartz diorites, emplaced at ca. 20-23 km, pass sequentially upward to porphyritic two-mica granodiorites

and granites, equigranular two-mica granodiorites and granites, biotite granodiorites and, finally, shallow fine-grained two-mica granodiorites and granites. As an added value, the Serre Batholith represents the intermediate portion of a nearly complete cross-section of late Variscan continental crust, continuously exposed from deep crustal metagabbros, equilibrated at c. 35 km depth, to upper crustal phyllites. The entire cross-section is exposed in the Serre Massif, but a significant portion of it, comprising the bottom magmatic units of the batholith and their underlying migmatitic host rocks, also crops out in the Capo Vaticano Promontory on the Calabrian Tyrrhenian coast (Cirrincione et al., 2015, and references therein).

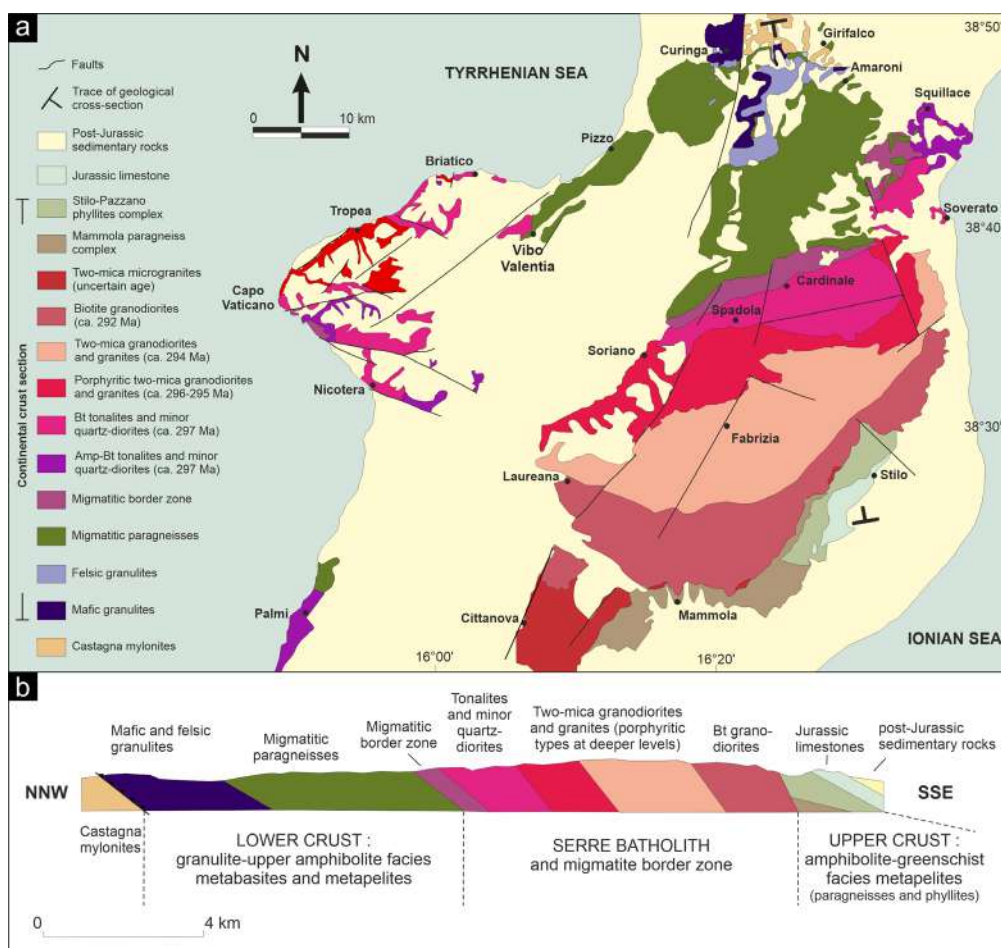


Figure 1 a) Geological overview map of the Serre Massif and Capo Vaticano Promontory (modified after Fiannacca et al., 2015; Ortolano et al., 2022; Russo et al., 2023). Granitoids ages after Fiannacca et al., 2017 and references therein. b) Simplified lithological cross-section of the Serre Massif (modified after Fiannacca et al., 2015).

Previous studies on the Serre Batholith have suggested that strongly foliated deep-seated tonalites and quartz diorites emplaced earlier at deep structural levels, whereas weakly foliated to undeformed tonalites, granodiorites, and granites would have emplaced later into higher crustal domains (Rottura et al., 1990; Caggiannelli et al., 1997; 2000). In addition, geochronological investigations have helped to define a general over-accretion model for the construction of the Serre Batholith, with younger granitoids being emplaced at progressively shallower depths (Langone et al., 2014; Fiannacca et al., 2017).

Nevertheless, solid constraints for elaborating a detailed model of the architecture and build-up mechanisms of the batholith are still missing. In particular, no structural-geological study aimed at investigating in depth the relationships between all the main magmatic units making up the batholith, as well as the specific field and microstructural features of each single unit, has been attempted so far.

In this framework, field investigations and mapping

activities represented the starting point of this research. They helped to define in detail the geological and structural features of the different magmatic units and clarify the relationships between them and the metamorphic basement. From this solid field base, further in-depth multidisciplinary studies have been performed.

More in detail, to investigate the link between magmatism and regional tectonics, thin-section analysis was focused on the deformation microstructures developed in Serre granitoids, outlining the deformation history associated with the construction and cooling of the batholith. Moreover, since most of the studied granitoids have not developed evident planar or linear fabrics, the AMS (Anisotropy of Magnetic Susceptibility) technique was employed, allowing the detection of an internal magnetic fabric also in the apparently isotropic granitoids. The obtained three-axis ellipsoid of magnetic susceptibility provided valuable information on the intensity and orientation of the deformation experienced by both the foliated and unfoliated rocks.

In particular, after a preliminary AMS study carried out

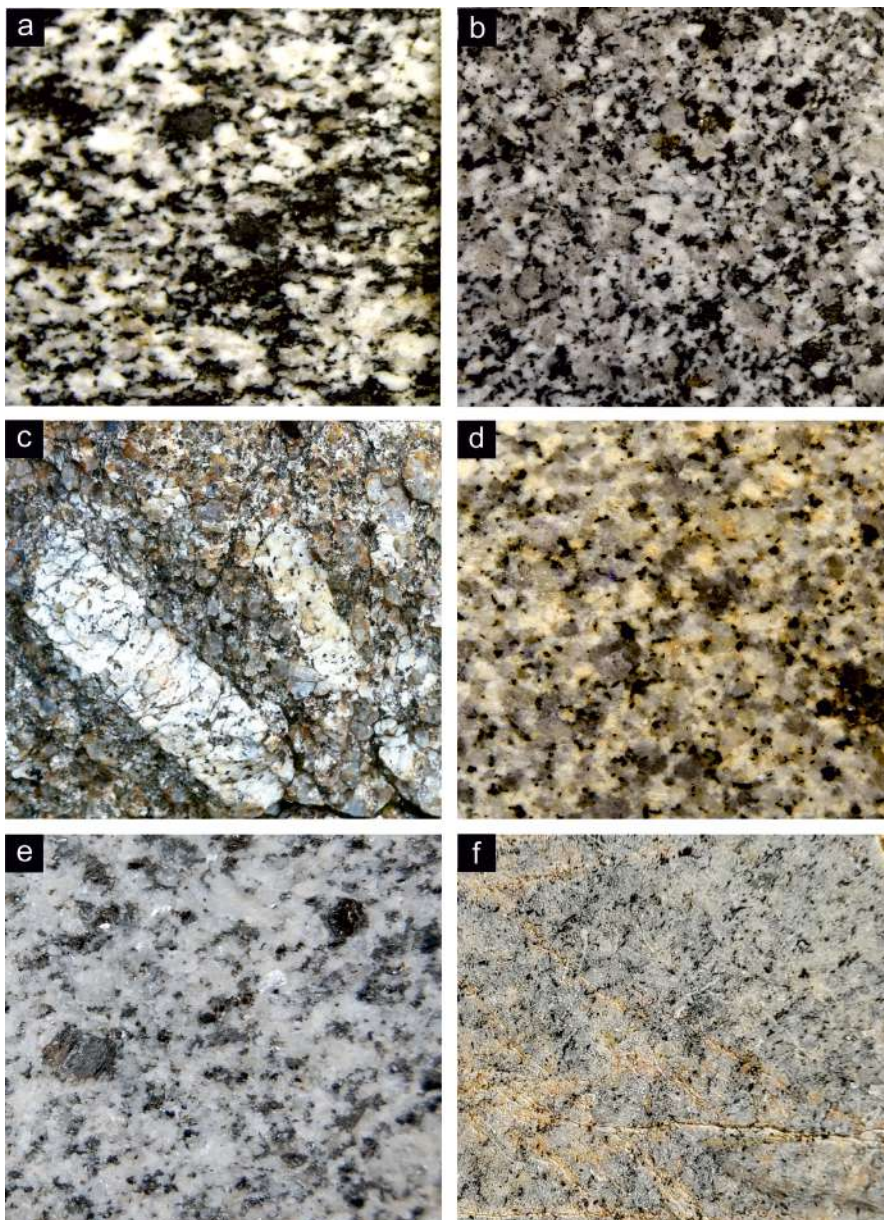


Figure 2 Mesoscopic comparison of floor (a) to roof (f) granitoids from the Serre Batholith. **a)** Moderately foliated ABT. **b)** Weakly foliated BT. **c)** Slightly oriented K-feldspar megacrysts in PMBG. **d)** Unfoliated MBG. **e)** Weakly foliated BG. **f)** Moderately foliated MBM. The long side measures 6 cm in all photos.

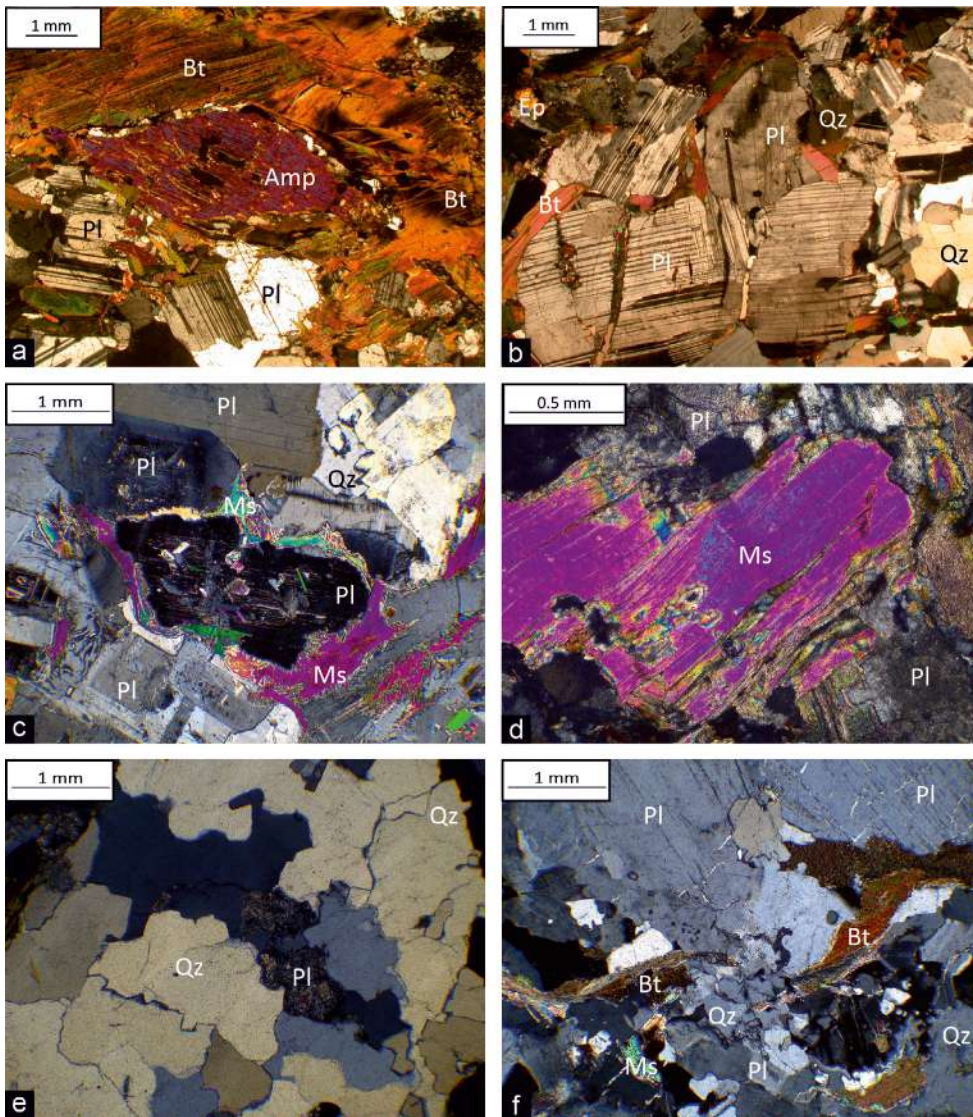


Figure 3 Deformation microstructures from submagmatic to solid-state regime in the granitoids from the Serre Batholith. **a)** Sigmoid amphibole, mantled by deformed biotite platelets and recovered quartz ribbons, suggests deformation at $T > 650^{\circ}\text{C}$ in ABT rocks. **b)** Several submagmatic microfractures, filled by subhedral biotite and epidote grains, in a large plagioclase crystal from BT rocks. **c)** Plagioclase bordered by asymmetrically anastomosing muscovite folia consistent with sub-simple shear deformation experienced by PMBG rocks. Myrmekites are also visible. **d)** Kinked muscovite in MBG rocks partly broken in smaller individuals with fish-like appearances. **e)** Well-displayed evidence of dominant GBM recrystallisation in a quartz domain from BG rocks. **f)** Well-developed oriented fabric marked by isoriented mica fishes in a strongly recrystallised micro-domain from MBM rocks. Large plagioclase crystals at the top exhibit muscovite-filled fractures oriented parallel to the mica fishes and subgrains testifying SGR recrystallisation in the crystal to the left.

by Fiannacca et al. (2021) on two magmatic units from the intermediate-upper crustal level of the Serre Batholith, the AMS investigations were here performed for the first time on all six magmatic units that represent the different growth stages of the batholith, from the deepest and oldest tonalites/quartz diorites to the shallowest and youngest two-mica microgranitoids.

Finally, the EBSD (Electron BackScattered Diffraction) technique has been additionally employed on selected samples from all the studied magmatic units, obtaining the first quartz Crystallographic Preferred Orientation (CPO) data for the Serre Batholith, aimed to: a) infer the intracrystalline deformation mechanisms and related slip-systems activation temperatures; b) reveal the deformation regime, i.e. coaxial vs non-coaxial; c) obtain possible kinematic constraints.

FIELD OBSERVATIONS

A robust field mapping, supported by petrographic investigations, revealed the relationships between all the main magmatic units making up the batholith, never mapped in such detail before this work. Strongly to moderately foliated amphibole-biotite tonalites (ABT; Fig. 2a)

and strongly to weakly foliated biotite tonalites (BT; Fig. 2b) represent the oldest and deepest granitoids. The BT have been further distinguished into strongly to moderately foliated (BTs) and weakly foliated to unfoliated (BTw), the latter typically occurring at the top levels of the BT unit. They transition upward to weakly foliated to unfoliated porphyritic muscovite-biotite granodiorites and granites (PMBG; Fig. 2c) by clear intrusive contacts, which are locally exposed. These observations refer to both the Serre Massif and Capo Vaticano Promontory sectors of the Serre Batholith. In particular, in the latter sector, where only the deep-intermediate portion of the batholith crops out, field activity and petrographic studies allowed to separate the promontory into a northern sector characterized by continuous exposure of the deep-intermediate granitoids and a southern sector with a more chaotic arrangement due to a stronger tectonic reworking.

The relationships between all the overlying magmatic units have been mapped and studied in the Serre Massif, where the whole cross section from floor to roof of the batholith is exposed.

The contact between PMBG and overlying unfoliated muscovite-biotite equigranular granodiorites and gran-

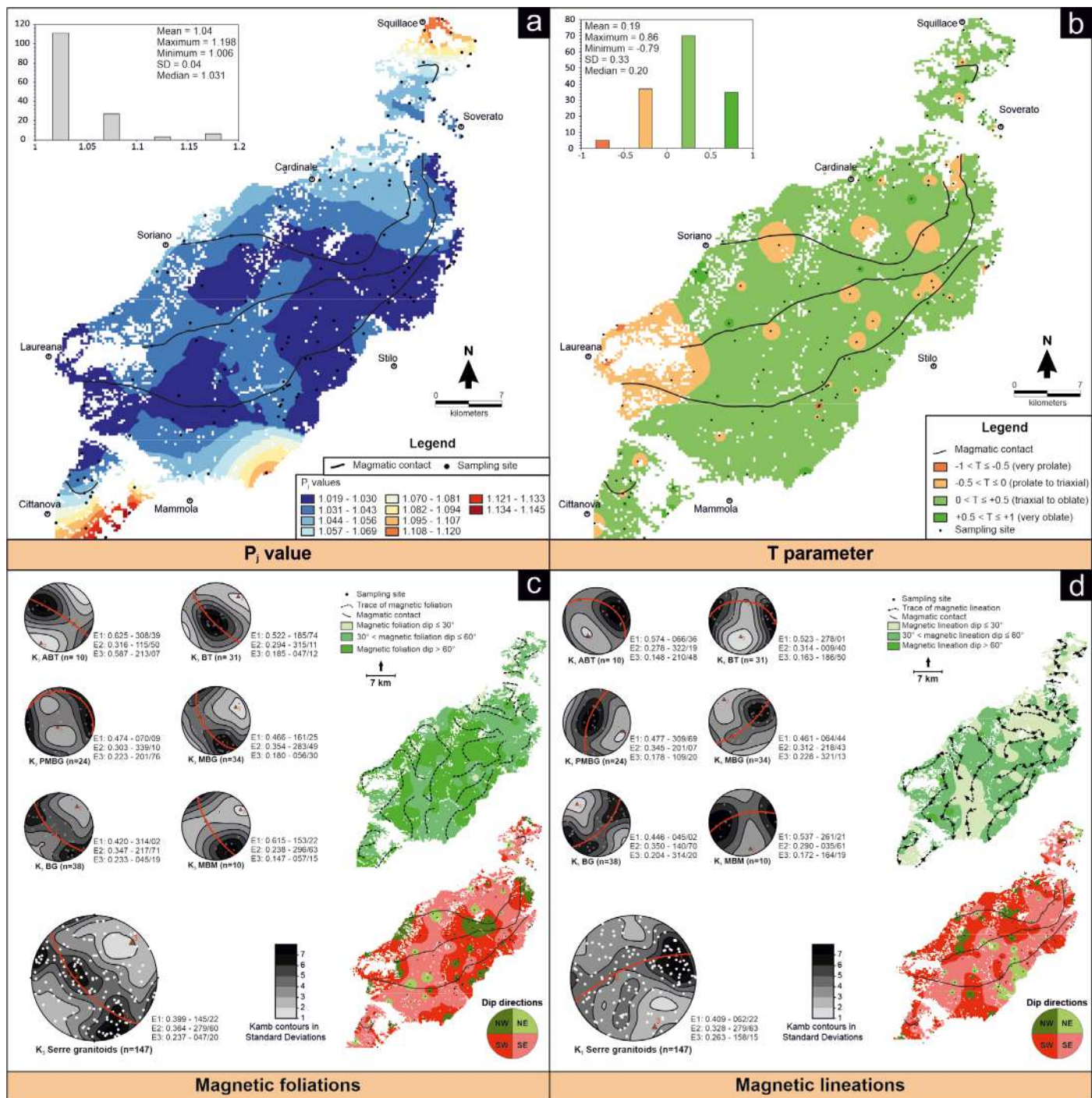


Figure 4 Representative histograms and contoured maps of **a**) the magnetic anisotropy and **b**) shape factor for the study area. Kriging and IDW interpolation methods have been employed in **a**) and **b**) contoured maps, respectively. **c**) Magnetic foliations and **d**) lineations data displayed using lower hemisphere equal area projections for the single magmatic units and the whole study area (on the left) and IDW-based interpolation maps (on the right). On the top right, **c**) magnetic foliation and **d**) lineation dip map with mean trajectories; on the bottom right, **c**) magnetic foliation and **d**) lineation dip direction map.

ites (MBG; Fig. 2d), as well as between the MBG and the overlying unfoliated to weakly foliated biotite granodiorites (BG; Fig. 2e), making up most of the batholith roof, is gradational, suggesting interaction of the newly emplaced granitoid magma with the largely solidified underlying unit. In addition, the BG unit is sharply intruded in its southwestern sector by fine-grained weakly to moderately foliated two-mica granodiorites and granites (MBM; Fig. 2f), which form the batholith roof in this sector.

DEFORMATION MICROSTRUCTURES

Microstructural investigations performed in all the CVP and Serre Massif magmatic units indicate deformation under active tectonic stress, with varying intensity recorded in the different units, from at least submagmatic conditions (Fig. 3a-f). However, a well-developed mineral preferred orientation in ABT-BTs and local weaker fabric in BTw-bottom PMBG, as well as in the BG and MBM from the southwestern sector of the Serre Massif, would indicate that the tectonic stress was already active at magmatic conditions. Suprasolidus deformation was followed by continuous subsolidus deformation at pro-

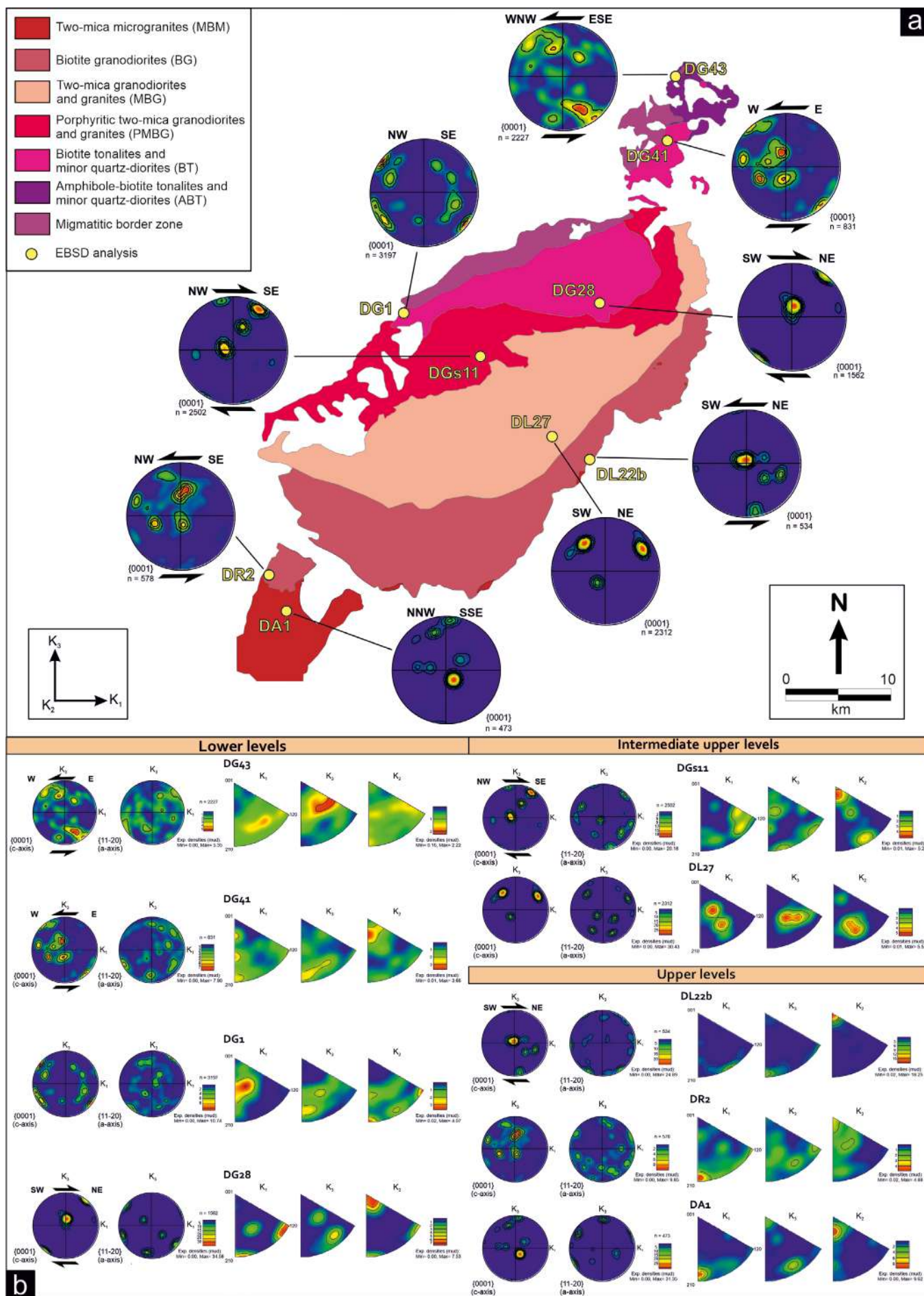


Figure 5 a) Distribution and mean orientation of quartz CPO fabrics in the Serre Batholith. For each oriented sample, quartz CPO was determined in thin sections cut parallel to K1K3 (parallel to magnetic lineation and orthogonal to the magnetic foliation). b) Graphical representation of EBSD data from the studied oriented samples of the Serre Batholith. The pole figures are plotted in the lower hemisphere, equal area, one point per grain of {0001} i.e., c-axis, and {11-20} i.e., a-axis of the quartz grains. N=number of quartz grains. The inverse pole figures are plotted in the upper hemisphere with a half width of 15° and a cluster size of 5° for each. Contour lines are multiples of uniform distribution (mud). EBSD analysis was carried out on thin sections parallel to the K1K3 plane of the AMS ellipsoid. The reference frame in all the diagrams is K1 (horizontal) and K3 vertical.

gressively lower temperatures during cooling of all the sequentially emplaced magmatic units, indicating uninterrupted tectonic activity during the batholith's lifetime. Stages of tectonic quiescence are, nevertheless, documented by static recrystallization microstructures (i.e., foam texture in quartz aggregates) showing evidence of tectonic reactivation (i.e., GBM and BLG dynamic recrystallization, stretched foam aggregates). Finally, kinematic indicators, more common in the ABT-BTs and top MBM (Fig. 3a, f), suggest deformation under a sub-simple shear regime.

ANISOTROPY OF MAGNETIC SUSCEPTIBILITY

Since many granitoids did not develop meso- and microscopic fabrics, AMS investigations were essential to identify an internal fabric also in the apparently isotropic granitoids. Granitoids are dominantly paramagnetic, with main magnetic carriers represented by biotite and local amphibole. The magnetic anisotropy (P_j ; Fig. 4a) increases in the deepest and shallowest units, suggesting possible magma emplacement along higher strain zones; lower P_j values in the intermediate-upper units are in accordance with a weaker tectonic activity during emplacement-to-cooling of these magmatic units. Similar low P_j values are nevertheless not rare in syn-tectonic granites. Prevailing oblate AMS ellipsoids are considered to reflect flattening of the emplacing plutons between the pre-existing underlying magmatic unit and overlying metamorphic host rocks, while minor prolate shapes, associated with sub-vertical lineations and foliations, might provide an indication of possible feeder zones (Fig. 4b). Magnetic foliations and lineations (Fig. 4c, d) reveal an extensional tectonic phase associated with emplacement of the oldest and deepest ABT unit and a dominant NW-SE compression direction for all the other units, consistent with tectonic stress mostly operating in a regional compressive regime during the construction of the batholith.

CRYSTALLOGRAPHIC PREFERRED ORIENTATION

Quartz CPO indicates deformation at medium to low temperatures, as suggested by dominant activation of basal $\langle a \rangle$, rhomb $\langle a \rangle$ and prism $\langle a \rangle$ slip systems (Fig. 5a, b). The absence of the c -slip system is here considered the result of superimposed lower temperature deformation. CPO asymmetric patterns recorded in most of the studied granitoid samples provide solid evidence for sub-simple shear deformation. Contrasting senses of shear obtained for rocks from different, or even the same, magmatic units might reflect minor conjugate shear planes associated with major shear zones activated during cooling of the granitoids or, alternatively, the

effect of superimposed post-Variscan deformation.

CONCLUDING REMARKS

This study, based on a multidisciplinary approach integrating field, microstructural, AMS and CPO data, allowed adding new significant constraints on the architecture of the late Variscan Serre Batholith and the link between batholith construction and activation of regional-scale shear zones. Dominant compression revealed by the AMS, coupled with the indication for shear-related deformation from kinematic indicators and CPO asymmetric patterns, is consistent with an active transpressional regime. Together with continuous supra- to sub-solidus deformation of varying intensity, these results indicate syn-tectonic magma emplacement of the studied granitoids, along a progressively waning shear zone.

This work proposes a multistage model to illustrate the architecture and the build-up mechanisms of the Serre Batholith (Fig. 6).

In such model, the magmatic units emplaced sequentially by incremental over-accretion along a shear zone. In particular, in the first construction stage, deepest ABT magmas emplaced syn-tectonically in a transtensional tectonic regime. On the other hand, the emplacement of the overlying units occurred in a transpressional regime, which operated throughout the build-up history of the batholith, triggering the nucleation of a crustal-scale shear zone, here named Lower Mammola Shear Zone (LMSZ), which detached the bottom of the Mammola Paragneiss Complex from the lower crustal metapelitic host rocks of the batholith.

From the top of the lower crust, the LMSZ started its rise to higher crustal levels, accommodating the newly emplacing magmatic units that were progressively sandwiched between the previously emplaced underlying granitoids and the overlying Mammola paragneisses, which acted as the continuously uplifted lid of the batholith. The LMSZ concluded its upward journey through the Calabrian crust at shallow crustal levels, in direct contact with the BG and MBM, representing the final stages of the Serre Batholith construction.

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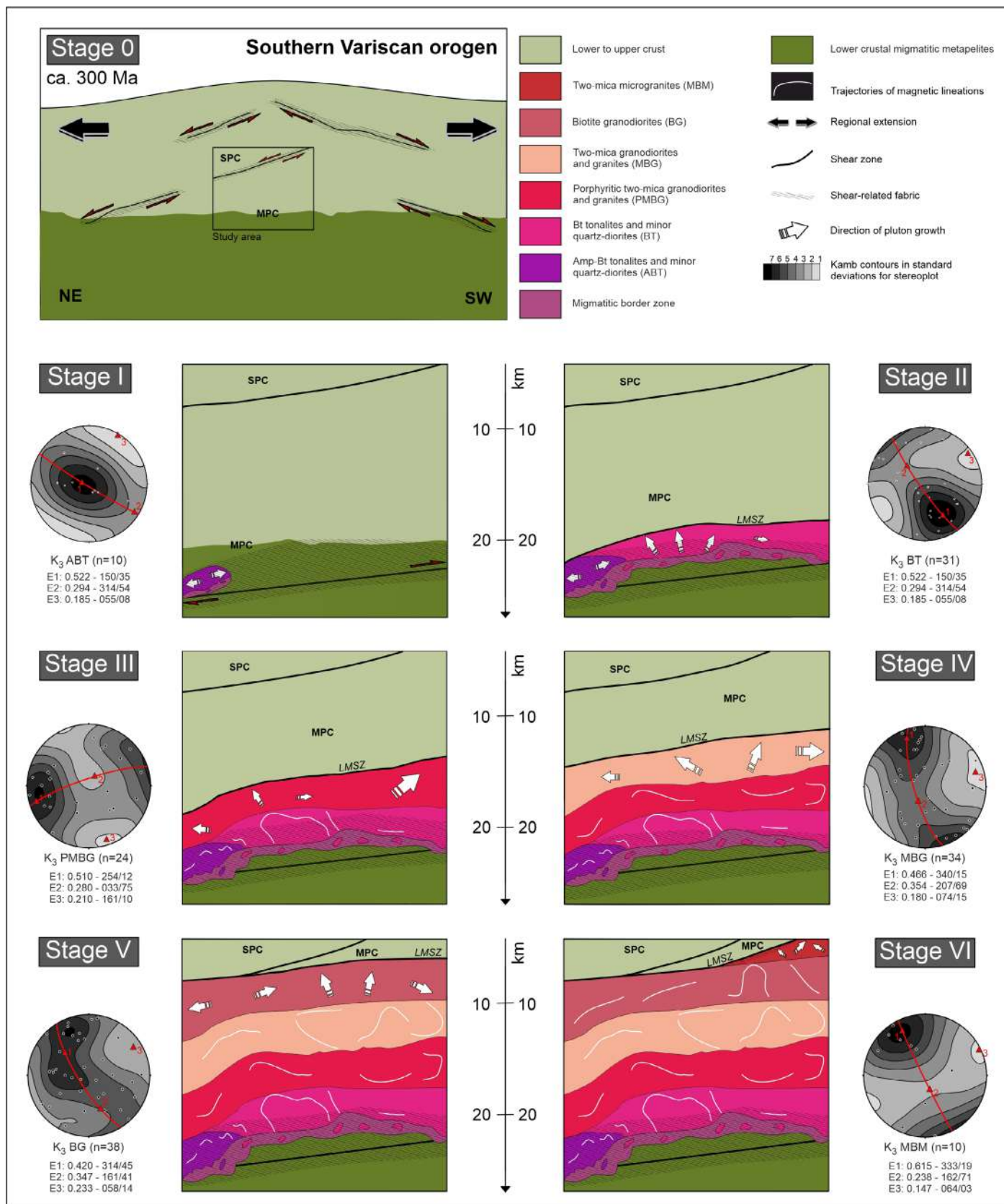


Figure 6 Simplified cartoon model illustrating the sequential stages of construction of the Serre Batholith in conjunction with stereoplots reporting poles of magnetic back-tilted foliations for each stage. Stage 0 represents the pre-emplacment scenario of the Serre Massif in the framework of the southern Variscan orogen. Stage I to Stage VI illustrate the sequential emplacement of the Serre magmatic units. See text for further details. SPC = Stilo Pazzano Complex; MPC = Mammola Paragneiss Complex; LMSZ = Lower Mammola Shear Zone. Hatched lines represent the inferred LMSZ in a progressively waning stage. Shown poles to magnetic foliations are tilted according to the original setting of the study area (i.e., 43° counterclockwise tilting looking in the direction of a N45° horizontal rotation axis; Festa et al., 2003). E1 corresponds to the far field principal stress axis; E2 equals to K2 axis of the magnetic ellipsoid; E3 is the magnetic lineation K1.

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SIMP Society Activities

80 | Distinguished Lectures 2024: IX ciclo di conferenze itineranti

81 | #SIMPWomenInSTEM

82 | Minerals as treasure trove for scientific discoveries

83 | Lake Como School of Advanced Studies: "Vibrational Spectroscopy Meets Geoscience (GeoVibrS)"

84 | Sustainability and risk: BeGEOscientists on the road to the future

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86 | GRANULITES & GRANULITES 2024

DISTINGUISHED LECTURES 2024: IX CICLO DI CONFERENZE ITINERANTI

Date: January-May 2024

Event link:

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Piero Gianolla (left) and Antonio Langone (right) during their lectures at the University of Torino.

Below, the event flyer.

The Distinguished Lectures are a series of traveling lectures organized by the Italian Society of Mineralogy and Petrology (SIMP) and the Italian Geological Society (SGI), where topics are examined from different perspectives by speakers presenting their innovative and critically provocative research. SIMP and SGI organize this joint initiative since 2012, aimed at stimulating critical interdisciplinary debate on topics in the Geosciences, organizing a tour of the Distinguished Lectures across Italy.

The theme of the Distinguished Lectures 2024 is: **“Quando e per quanto tempo? La variabile tempo nelle geoscienze, dal record geologico alla sfida analitica”**. The speakers have visited six departments/research institutions: Milan, Turin, Potenza, Padua, Florence and Trieste.

During the Distinguished Lectures 2024, Piero Gianolla (University of Ferrara) contributed a lecture titled **“Ricostruire il Tempo Profondo: riflessioni dal Triassico delle Dolomiti”**, presenting one of the most spectacular and unique examples of geological time records in the world, the Dolomites. In his seminar, Piero demonstrated all the approaches for reconstructing a continuous and extensive stratigraphic sequence like that of the Dolomites, both relatively and absolutely.

Antonio Langone (University of Pavia) presented **“Dalla geocronologia alla petrocronologia: la brama del vincolo temporale nelle Geoscienze”**, focused on the history of the evolution of geochronology, from the discovery of radioactivity to the present day, highlighting new and future approaches in isotopic geochronology.

Antonio and Piero described it as a unique experience. They told Plinius that presenting ‘Geological Time’ and the various approaches to quantifying it, from the perspectives of two experts with diverse yet complementary skills, was highly educational for both themselves and the entire audience.



IX CICLO di CONFERENZE ITINERANTI

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Società Geologica Italiana e Società Italiana di Mineralogia e Petrologia hanno il piacere di annunciare un'iniziativa congiunta che ha lo scopo di stimolare un critico dibattito interdisciplinare su tematiche delle Geoscienze. Le Distinguished Lectures sono una serie di conferenze itineranti, la cui tematica è vista da prospettive differenti da parte di conferenzieri che presenteranno loro ricerche innovative e criticamente provocatorie. Le due conferenze verranno tenute congiuntamente e sono rivolte a studenti, dottorandi, assegnisti e ricercatori.

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Frames from the video interviews available at the above links.

Stefania Corvò, postdoc researcher at the University of Pavia, combines notions of structural geology with metamorphic petrology. In addition to research, she is involved in extra activities such as science outreach and teaching and won numerous awards including the SIMP Study Abroad Scholarship Award. For her, being a geoscientist means putting yourself on the line every day. Fortunately, she works with a teamwork that enhances her professional and personal skills.

Message to young female geoscientists: *If there is passion and curiosity, you are on the right track. Never give up, the obstacles themselves are a lesson in life, with determination the sacrifices will be rewarded, and experience tells us so.*

Chiara Anzolini, researcher at the University of Padova and member of National Secretary of ADI (Associazione Dottorandi e Dottori di Ricerca In Italia), won the best Doctoral Thesis award from SIMP in 2018. She moved onto science communication with a master's degree in Trieste. Gender equality in STEM is a topic she has been passionate about for many years. During her Master's she won a grant from the municipality of Trieste to create together with secondary school classes a podcast on the gender gap in STEM. The podcast is called "TrieSTEM - Let's give female scientists a voice" and can still be found on podcast platforms.

Message to young female geoscientists: *The precarious research world is not the only way, fight for your future.*

Nadia Malaspina, associate professor at the University of Milano-Bicocca, is the former SIMP treasurer and current SIMP secretary. She deals with gender issues at University and orientation activities enabling girls to get involved in STEM disciplines. She is involved in a working table that collaborates with the equal opportunities observatory of Bicocca university to implement initiatives and actions to be carried out by the "Gender Quality Plan", an epoch-making reform by the EU, allowing the university to take concrete action on the employment gap.

Message to young female geoscientists: *Continue to cultivate your passions, aware that in the world of work and academia, even if we are women, we have the same opportunities of man and we must overcome the psychological barriers that limit women's career opportunities.*

Stefania and Nadia expressed their gratitude to SIMP in a note to Plinius for the opportunity to share their experiences, passions, work, and opinions in the field of geosciences and as geoscientists.

MINERALS AS TREASURE TROVE FOR SCIENTIFIC DISCOVERIES

Date: 15-16 February 2024

Event link:

<https://www.lincci.it/it/manifestazioni/minerals-treasure-trove-scientific-discoveries>

*Giorgio Parisi opening message
for the beginning of the
Conference.*

Minerals have been of great interest not only to nature scientists but to chemists and physicists too. The meeting was an occasion to put together renowned scientists with different backgrounds to underline once more time the importance of minerals in scientific research.

The event had 80 in-person participants and an additional 100 participants joining virtually.

The SIMP offered a grant of 1000€ for travelling / accommodation expenses for junior SIMP delegates. Thus, 9 grants were attributed during this event, and the names of the winners are listed below:

Mattia Sisti, Francesco Colombo, Marta Morana, Alice Taddei, Daniela Mauro, Lisa Baratelli, Riccardo Fantini, Lorenzo Barni, Antonio Ciccolella.



As said in the welcome message, the main Coordinator of the meeting, Luca Bindi, thanked the Italian Society of Mineralogy and Petrology for the grants that allowed the participation of nine young students at the meeting. Thanks to the Society Committee and especially to the President of the Society Paolo Mazzoleni.

Organising Committee: Vincenzo AQUILANTI (Linceo, University of Perugia), Luca BINDI (Coordinator, Linceo, University of Firenze), Gilberto ARTIOLI (University of Padova), Maria Franca BRIGATTI (Lincea, University of Modena and Reggio Emilia), Giovanni FERRARIS (Linceo, University of Torino), Massimo INGUSCIO (Linceo, University Campus Biomedico of Roma), Stefano MERLINO (Linceo, University of Pisa), Giovanni MODUGNO (University of Firenze), Annibale MOTTANA (Linceo, University Roma Tre), Roberta OBERTI (Lincea, Institute of Geosciences and Earth Resources - CNR Pavia), Roberta SESSOLI (Lincea, University of Firenze).



*A shot of the audience in the
venue of Palazzo Corsini in
Rome.*

Vibrational spectroscopic techniques are increasingly essential for the in situ investigation of Earth's and planetary materials at the microscale, as they preserve the pristine nature of the samples during analysis. However, recent advancements in these techniques are pushing the limits of data interpretation and processing, which now require more integration with computational methods. In Earth Sciences, we are evolving from the basic 'measure-compare' approach to a more nuanced 'simulate-measure-interpret' methodology.

The school, which featured 15 leading scientists delivering lectures and hands-on practical courses, saw an overbooked attendance of 45 participants, surpassing the venue's maximum capacity. Registrations came from master's students, PhD students, and junior researchers from eight countries: Italy, France, the United States, Spain, Germany, Poland, Austria, and Croatia. Practical sessions on the fourth day included the use of a Raman spectrometer, and students had the opportunity to present their work through posters or short talks. The final day concluded with a round table for students to share their ideas and experiences from the school.

The SIMP generously supported the school with four grants covering the cost of attendance. The recipients of these grants were Lisa Baratelli (University of Milano), Giulia Mingardi (École Normale Supérieure Paris), Sara Monico (University of Milano), and Lorenzo Pasetti (University of Parma).

Matteo Alvaro, one of the co-organizers, conveyed his gratitude to SIMP for their support on behalf of the organizing committee and the students who benefited from the grants, in a note to the journal *Plinius*.

Organizing Committee: Fernando CAMARA (Professor of Mineralogy and Crystallography, Department of Earth Sciences "Ardito Desio" University of Milano, Italy), Matteo ALVARO (Professor of Mineralogy and Crystallography, Department of Earth and Environmental Sciences, University of Pavia, Italy), Marco SCAMBELLURI (Professor of Petrology Department of Earth Sciences, Environment and Life, University of Genova, Italy).

LAKE COMO SCHOOL OF ADVANCED STUDIES: "VIBRATIONAL SPECTROSCOPY MEETS GEOSCIENCE (GeoVibrS)"

Date: 24-28 June 2024

Event link:

<https://geovibrs.lakecomoschool.org/>

[lakecomoschool.org/](https://geovibrs.lakecomoschool.org/)



The flyer of the School.

SUSTAINABILITY AND RISK: BeGEOscientists ON THE ROAD TO THE FUTURE

Date: 3-6 October 2023

Event link:

<https://www.begeos.it/>

The flyer of the Conference.

The BeGEO Scientists Association and Project were founded by a group of students and PhD students in Earth Sciences with the goal of creating a network of young researchers for young researchers as a way to share their own experiences and knowledge. In recent years, BeGEO has organized events of national and international significance, providing participants with the chance to present their work and interact with researchers and colleagues worldwide.



Both editions of the BeGEO Congress for Young Geoscientists, the first in 2021 and the second in 2023, were very well-received, counting a significant number of participants from all around Italy as well as a discreet percentage of foreign PhD students from around the world; the last edition was articulated in 16 sessions, for a total of about 170 contributions and with nearly 300 young participants eager to share their experiences and knowledge in a multidisciplinary environment.

The BeGEO Scientists Association reports that all objectives have been achieved thanks to the trust placed in them, which was crucial for the event's success. SIMP's generous contribution encouraged young geoscientists to join their network, established four years ago. Collaboration with Plinius allowed them to publish the participants' extended abstracts in the SIMP official bulletin, enhancing the visibility of their contributions and encouraging further participation.

Four travel grants of €250 each were awarded to the best presentations. The recipients were Lorenzo Dulcetta (University of Cagliari), Mattia Bonazzi (University of Pavia), Sara Nerone (University of Torino), and Silvia Portale (University of Catania).

In a note to Plinius, the BeGEO Scientists Association expresses its gratitude for the support of SIMP and the staff of Plinius journal.

(Left) A shot of the participants in the hall of the Department of Earth Sciences, Environment and Resources of the University of Napoli - Federico II.

(Right) The BeGEO Organising Committee.



Below, from left to right, Sara Nerone, Lorenzo Dulcetta, Mattia Bonazzi and Silvia Portale, winners of the SIMP travel grants.



emc²

18–23 August
2024

4th european mineralogical
conference • Dublin, Ireland

EMC2024 4TH EUROPEAN MINERALOGICAL CONFERENCE

Date: 18-23 August 2024

Event link:

<https://emc-2024.org/>

The organizing committee, in collaboration with the Mineralogical Society of the UK and Ireland, successfully hosted the 4th European Mineralogical Conference (EMC2024) in Dublin. The conference aimed to foster the exchange of new research results among European countries, a goal that has been effectively pursued through previous events in Frankfurt, Rimini, and Krakow.

This year's conference featured several field trips to notable locations, including Glendalough, Co. Wicklow; Giant's Causeway, Co. Antrim; Slieve Gullion, Co. Armagh; Ireland's Collections Resource Centre; and Howth Head, Co. Dublin. These trips provided attendees with opportunities to explore various aspects of Ireland. Additionally, a number of short courses were offered, focusing on Quantitative Microanalysis Synchrotron Techniques, with a specific emphasis on environmental topics and Phreeqc. A range of social events, welcoming family members, complemented the conference schedule. Pre- and post-conference activities also offered a variety of attractions.

The conference included two in-person poster sessions and four days of oral sessions. Notable plenary speakers featured were Luca Bindi, Patricia Dove, Jakub Kierczak, and Catherine McCammon. Approximately thirty-eight sessions were proposed and organized, covering a broad spectrum of topics including petrology, mineralogy, applied mineralogy, analytical experimental techniques, and geomicrobiology. Specific topics included archeometry and cultural heritage, planetary sciences, geochemistry, critical metals, and the Circular Economy. Sessions also addressed education, science communication, and women in geosciences.

The SIMP supported the conference by announcing four grants for student attendance.

Organizing Committee: Emma Tomlinson, David Chew and Kevin Murphy and sponsors (see image below).



GRANULITES & GRANULITES 2024

Date: 3-6 September 2024

Event link:

<https://granulites2024.sfmc-fr.org/>

An intergrowth "symplectite" of golden pyroxene and blue plagioclase replacing garnet in a mafic granulite from Manitoba, Canada. Credit MicROCKScopica

The Maggiore Conference Center in Verbania, venue of the Conference



Granulites & Granulites 2024

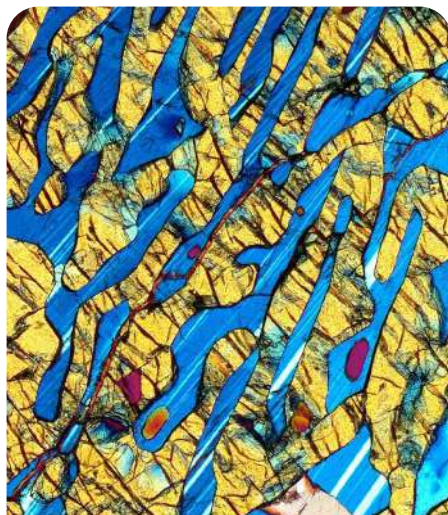
This international conference focuses on high-temperature processes in the middle and lower crust, including migmatite and granulite formation, crustal anatexis, melt extraction and transfer, structure and composition of the lower crust, and crust-mantle interactions.

Mid-conference activities will offer several different options for attendees:

1. Walk across the Moho from mantle peridotite through pyroxenite and gabbro to crustal granulite;
2. Visit to the spectacular Candoglia marble quarry, used to build the Duomo in Milan;
3. Scientific workshop "Phase Equilibrium Modelling with MAGEMin". This workshop will introduce delegates to the phase equilibrium modelling software MAGEMin and associated thermodynamic models;
4. Visit to the picturesque Botanical Garden and Villa Taranto in Verbania.

The conference will be also accompanied by pre- and post-conference field trips: i) a pre-conference field trip to the archetypal continental crust-upper mantle section of the Ivrea Zone, Italy; ii) a post-conference field trip to the Variscan continental crust of southern Calabria, including the Serre Massif, Italy; and iii) a post-conference field trip to the classical sites of the southern and central Alps (Finero, Southern Steep Belt and Alpe Arami, Italy and Switzerland).

The conference will be attended by 135 participants. Keynotes will be delivered by: Nathan Daczko (Macquarie University, Australia), Shujuan Jiao (Chinese Academy of Sciences, China), Barbara Kunz (The Open University, UK), Andy Smye (Pennsylvania State University), Olivier Vanderhaeghe (Univ. Toulouse, France), Chris Yakymchuk (Univ. Waterloo, Canada).



Invited speakers also include: Emilie Bruand (Univ. Brest, France), Bruna Carvalho (Univ. Padova, Italy), Luca Mene-gon (Univ. Oslo, Norway), Jean-François Moyen (Univ. Saint Etienne, France), György Hetenyi (Univ. Lausanne, Switzerland).

Granulites & Granulites 2024 will be kindly sponsored by the Società Italiana di Mineralogia e Petrologia, which is offering two grants of 500 euro each in support of the participation to the conference of two SIMP Junior members.





Photo Contest Submissions

Here are all the submissions of the SIMP members to the photo contest, with the theme "**STRANGER THINGS - hidden faces from macro to microscale**" held to decide the image that is being featured on the cover of this issue.

A commission of experts has appointed
"Urlo di Munch" by **Silvia Favaro**
as the winner of the contest.

Here onward, the photos are displayed according to the submission order

Urlo di Munch



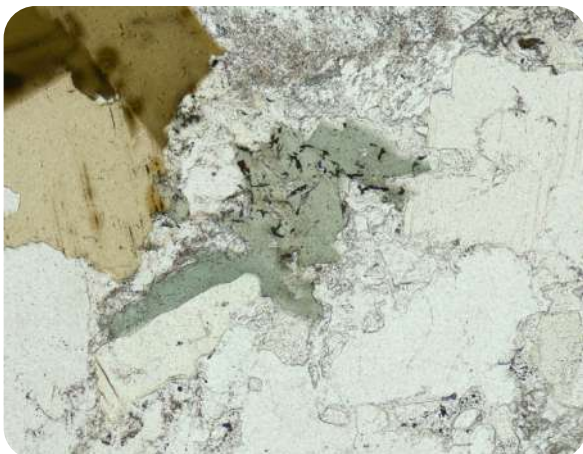
#1 Lorenzo Sedda



#2 Silvia Favaro

Il simbolo dell'anno è il dragone

Memorable thin section - scared face detection

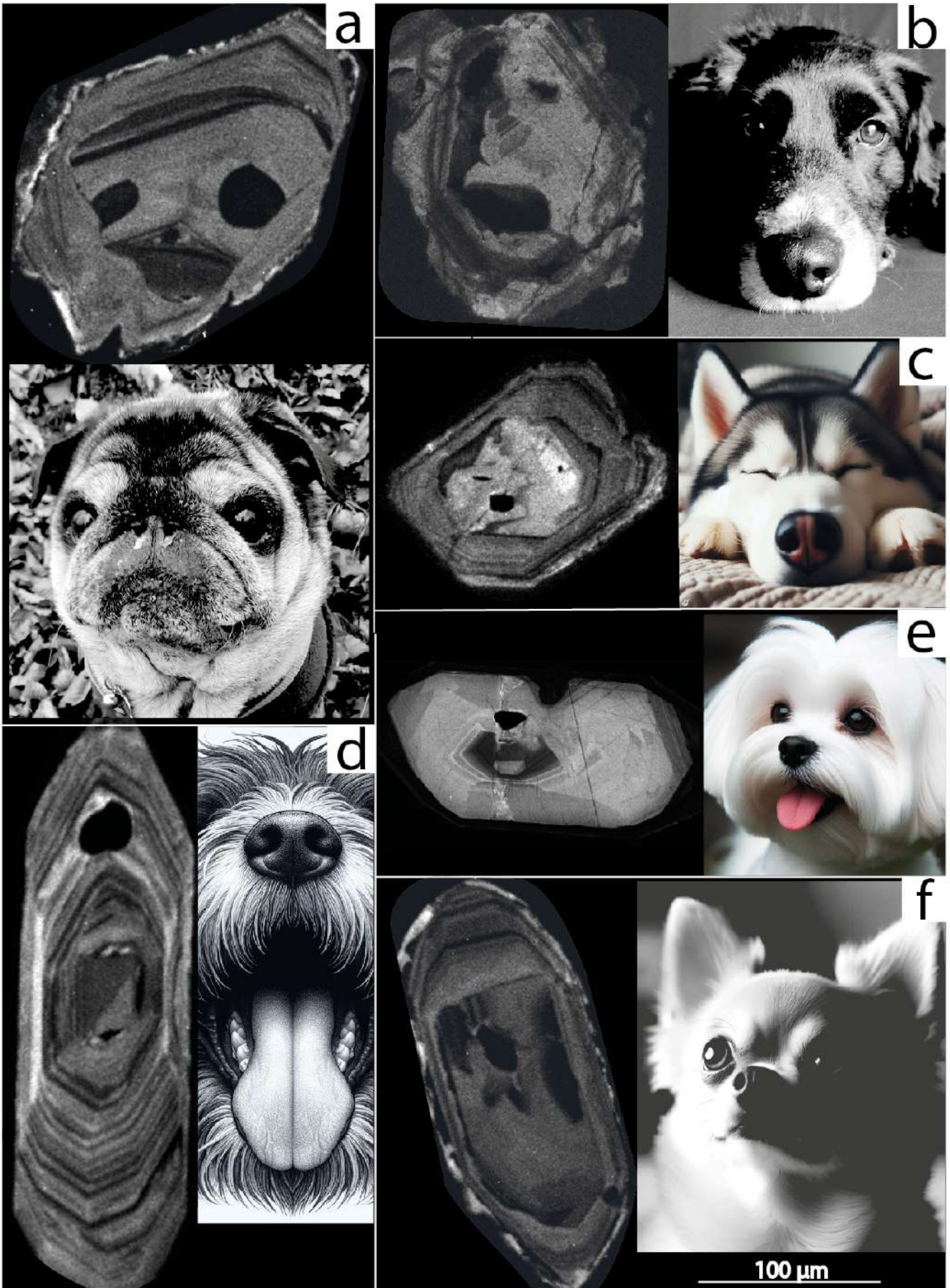


#3 Olga Demina



#4 Veronica Stopponi

Zircanis, a new enigmatic living mineral species from the Adamello Batholith



#5 Silvia Favaro

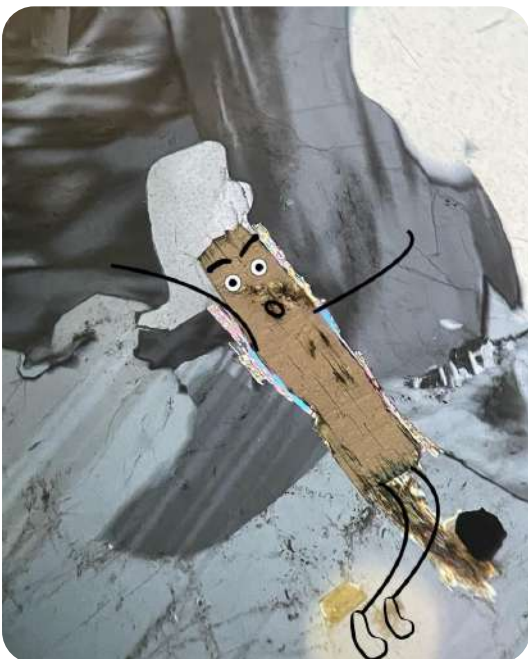
The Deep Sight of Sulfur



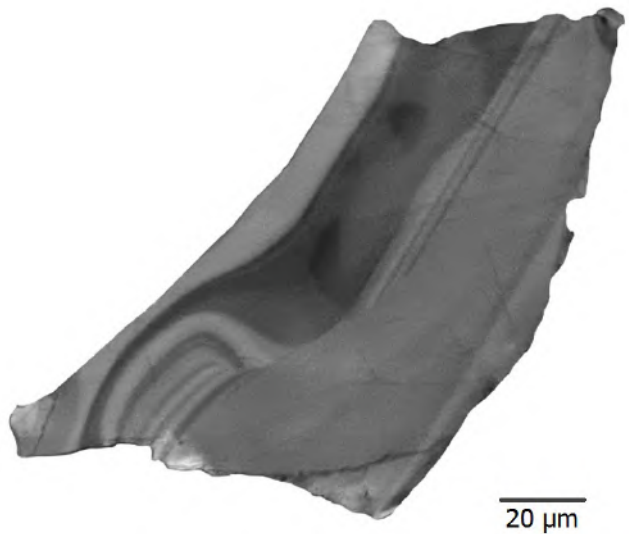
#6 Matteo Masotta

“Foetal” zircon exhibiting human-like facial features

BIOTITE PRESLEY



#8 Francesca Genova



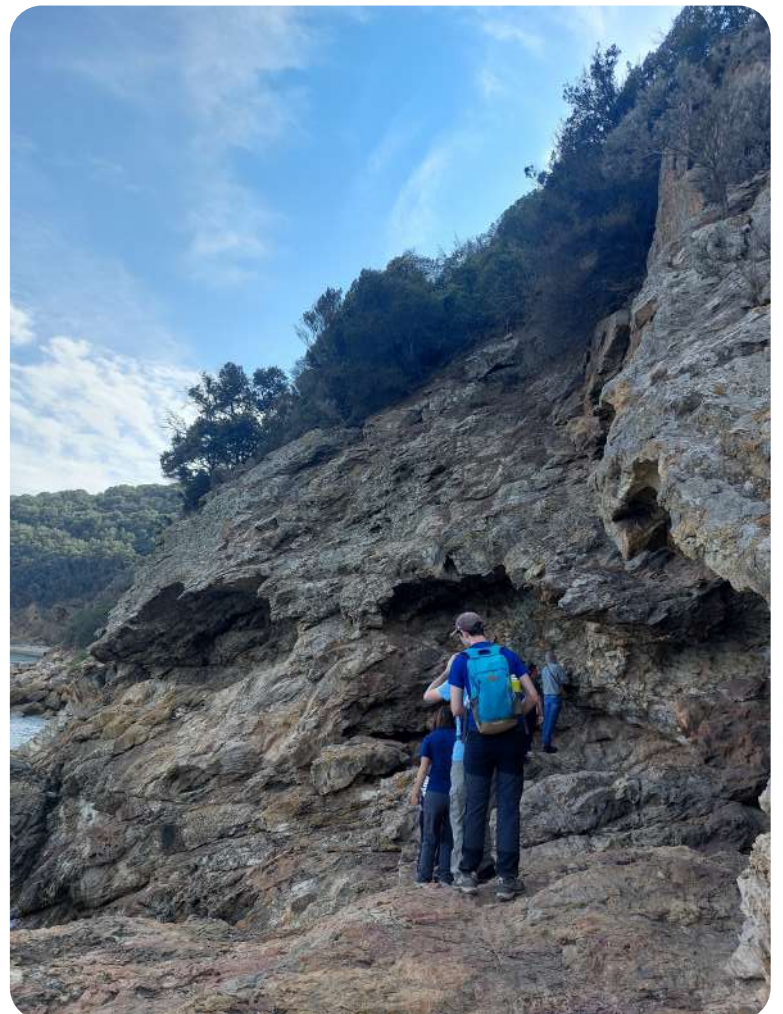
#7 Abimbola Chris Ogunyele

Skull of rock



#9 Giovanni Fanelli

The curse of Elba Island



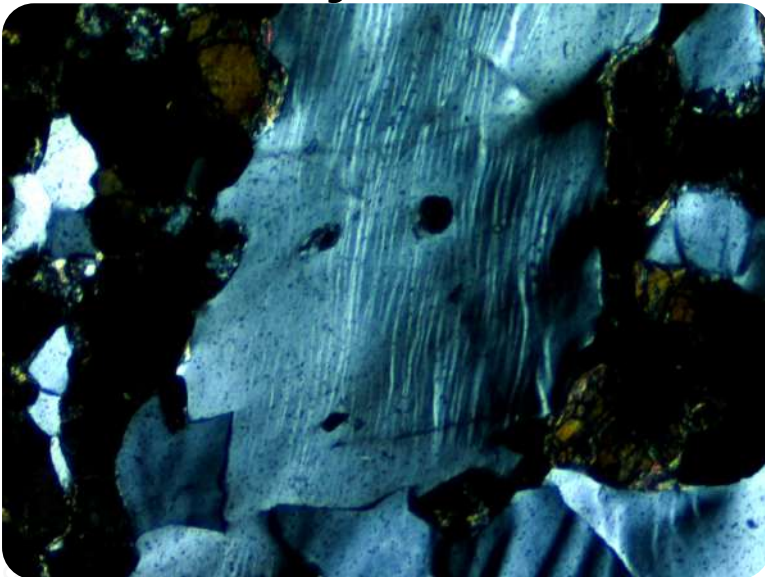
#10 Giovanni Fanelli

Love is in the... rock



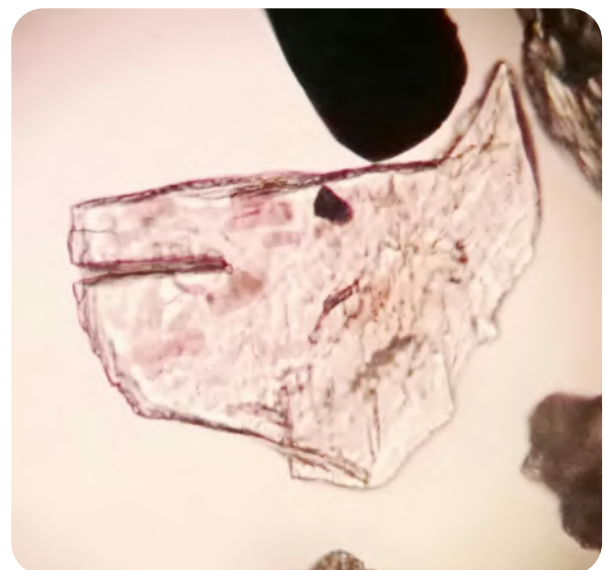
#11 Antonio Angellotti

Is it really so hot here?



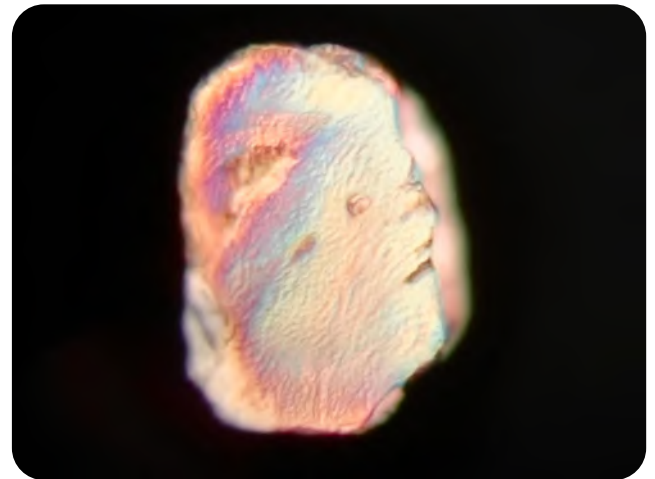
#12 Fabiola Caso

A wolf in a grain of sand



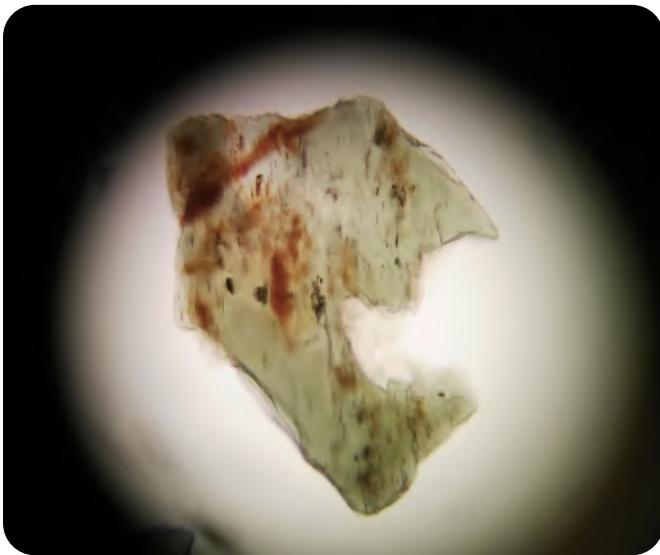
#13 Sergio Andò

A ghost imprisoned in a grain of sand



#14 Sergio Andò

The laughing witch



#15 Sergio Andò

The scary Hornblende



#16 Sergio Andò

- Lorenzo Sedda** (*University of Cagliari*) - "Micropiante" su microminerali della miniera di Santa Lucia (Fluminimaggiore - Sardegna SW).
- Silvia Favaro** (*University of Milano-Bicocca*) - **Urlo di Munch** - Aplitic dyke (Sierra Nevada Mountains, California).
- Olga Demina** (*Nature Research Centre*) - **Il simbolo dell'anno è il dragone** - Foto al microscopio. La clorite sostituisce la biotite nella roccia granitica.
- Veronica Stopponi** (*CNR - Institute of Materials - IOM*) - **Memorable thin section - scared face detection** - Singolare particolare al microscopio della sezione sottile capitatami durante un'esercitazione del corso Melting & Volcanism, risalente ai tempi del mio periodo Erasmus alla UCL di Londra, marzo 2017.
- Silvia Favaro** (*University of Milano-Bicocca*) - **Zircanis, a new enigmatic living mineral species from the Adamello Batholith** - Zircanis, ideally $ZrSiO_4$ (DOHG), is a new mineralized living form from the Adamello Batholith, resembling, as viruses, organisms at the edge of life. The mineral is named after zircon, its most common pseudomorph, and the latin term canis, of which Zircanis is the smallest species ever discovered. CL analysis reveal Zircanis specimen within magmatic crystals as restitic cores of about 50-100 μm in size. CL analysis were performed at the University of Milano (EMPA) and the University of Padova (SEM). Canis familiaris images were donated by (A) O. Bartoli; (B) F. Vergani and (C-F) were created using Bing AI.
- Matteo Masotta** (*University of Pisa*) - **The Deep Sight of Sulfur** - Inclusioni fluide in vetro silicatico contenenti cristalli di zolfo, sintetizzate ad alta pressione-alta temperatura.
- Abimbola Chris Ogunyele** (*University of Pavia*) - **"Foetal" zircon exhibiting human-like facial features** - The image shows a zircon crystal with internal structures mimicking the facial features of a human foetus. From the top-left to the bottom-left, it is possible to see a human-like head with an eye, mouth and "thin" neck. The photo is a SEM-BSE image taken at the CNR-IGG Pavia.
- Francesca Genova** (*University of Padova*) - **BIOTITE PRESLEY** - Questo minerale di biotite è il più grande fan di Elvis Presley. Ama indossare una parrucca di quarzo e riprodurre le iconiche mosse del cantante. La sua canzone preferita è "Blue suede shoes".
- Giovanni Fanelli** (*University of Bari "Aldo Moro"*) - **Skull of rock** - Frammento litico con inclusioni di sezioni basali di Anfibolo (Hbl) che vanno a determinare le cavità oculari e nasale del teschio. Sezione sottile ottenuta da campioni prelevati dalla formazione delle Tufiti di Tusa di Canale Candela - Rotondella (MT) - Basilicata.
- Giovanni Fanelli** (*University of Bari "Aldo Moro"*) - **The curse of Elba Island** - Affioramento sulla costa dell'Elba che sembra disegnare un volto che si eleva dal mare. Escursione prevista nel corso di Geodinamica del Mediterraneo - Prof. Liotta Domenico e Prof. Brogi Andrea (Dipartimento di Scienze della Terra e Geoambientali di Bari - DiSte-Geo).
- Antonio Angellotti** (*Sapienza University of Roma*) - **Love is in the... rock** - Sezione sottile di una Malta Romana con un cuore di Olivina - Foto da Antonio Angellotti e Beatrice Schiavon.
- Fabiola Caso** (*University of Milano*) - **Is it really so hot here?** - "Face" of a feldspar warmed up for the high temperature is experiencing within a basic granulite from the Valpeltine Series in the Western Alps.
- Sergio Andò** (*University of Milano-Bicocca*) - **A wolf in a grain of sand** - This is a grain of sand photographed under an optical microscope, in transmitted light. It is part of the heavy mineral suite mounted with Canada balsam on a slide. It is identified as an orthopyroxene from the Limpopo River, Mozambique. The shape is the result of crystallographic features, inclusions and my fantasy.
- Sergio Andò** (*University of Milano-Bicocca*) - **A ghost imprisoned in a grain of sand** - This is a grain of sand photographed under an optical microscope, in transmitted light with crossed Nicol. It is part of the heavy mineral suite mounted with Canada balsam on a slide, and it is identified as a diopsidic clinopyroxene from the Orange River, South Africa. The texture is the result of a slight corrosion due to chemical and physical weathering.
- Sergio Andò** (*University of Milano-Bicocca*) - **The laughing witch** - This is a grain of sand photographed under an optical microscope, in transmitted light. It is part of the heavy mineral suite mounted with Canada balsam on a slide, and it is identified as a Ca-Hornblende from the Kagera River, Rwanda. The texture is the result of a severe corrosion due to chemical weathering, a deep bay with etch pits is well developed.
- Sergio Andò** (*University of Milano-Bicocca*) - **The scary Hornblende** - This is a grain of sand photographed under an optical microscope, in transmitted light. It is part of the heavy mineral suite mounted with Canada balsam on a slide, and it is identified as a Ca-Hornblende from the Nyabarongo River, Rwanda. The texture is the result of an intense corrosion due to chemical weathering, two holes look like eyes and a deep horizontal cavity mimics the grin of a mouth in this scary hornblende.

Zircanis, a new enigmatic living mineral species from the Adamello batholith

Favaro, S.¹, Risplendente, A.² and Sessa, G.²

¹ University of Milano-Bicocca; ² University of Milano

ABSTRACT

Zircanis, ideally $ZrSiO_4(DOH)_2$, is a new mineralized living form from the Adamello batholith, resembling, as viruses, organisms at the edge of life. The mineral is named after zircon, its most common pseudomorph (Snoopy, 2015), and the Latin term *canis*, of which *Zircanis* is the smallest species ever discovered.

DATA

We collected 19 samples from the Adamello batholith and in only two we found *Zircanis*. Usually it occurs as single subhedral crystals, relatively free from inclusions, that rarely exceed 50-100 μm in size. It is associated with quartz, feldspar and, more often, labradorite and wolframite. *Zircanis* is opaque, with a velvet lustre and has a Mohs' hardness of 1, very soft. In plane-polarized reflected light, the mineral is dark and has abundant white internal reflections, but with cathodoluminescence (CL) technique it shows a patchy xenocrystic core, always resembling a dog face shape, mantled by newly grown fibrous material, called fur (Fig. 1). Chemical analysis

reveal the presence of organic carbon in the form of DNA within the dark patches of the restitic core. It usually contains trace amount of Ho, U, Nd.

DISCUSSION

The special properties of the organic compounds, combined with its morphological and morphometrical CL analysis, suit *Zircanis* into the Chordata phylum as the smallest known mammal. A new U/Pb analysis obtained with LA-ICP-MS yield an age of 900 Ma, making *Zircanis* the first dog on earth. This is in contrast with the most recent studies on well-preserved remains of early domestic dog (*Canis familiaris*) which gives ages all ranging between the late Glacial and early Holocene periods (ca. 14-9 ky BP), with few putative dogs found prior to the Last Glacial Maximum (ca. 27-19 ky BP; Clutton-Brock, 2016). Moreover, we could link its formation at the origin of prebiotic molecules. The three most popular hypotheses of their appearance are: synthesis in a reducing atmosphere, input in meteorites and synthesis of *Zircanis* minerals in the middle crust at depth of 8 -10 km within a convergent geodynamic setting. Projecting the Darwinian principle of evolution by selection of the fittest backwards into the Archean (Darwin, 1859), where the first living beings are supposed to have developed, *Zircanis*-like crystallization is one of the most reliable hypothesis of the origin of life, as cuteness is one of the major feature for survival. This newly discovered formation mechanism could hasten the origin of life back into the Hadean Eon.

CONCLUSION

CL analysis reveals *Zircanis* specimen within the magmatic crystal as a restitic core of about 50-100 μm in size. Chemical analysis confirmed the presence of DNA which, taken together with its CL phenotypic characteristics and U/Pb 900 Ma age, makes *Zircanis* the smallest and oldest living dog on Earth. Moreover, *Zircanis* crystallization mechanism could hasten the origin of life back into pre-Archean times.

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- Darwin, C. (1859) - On the Origin of Species by Means of Natural Selection, or the Preservation of Favoured Races in the Struggle for Life. John Murray, London.
- Snoopy, B. (2015) - Zircon - *Zircanis* phase diagram. J. Min. Bio., 6.

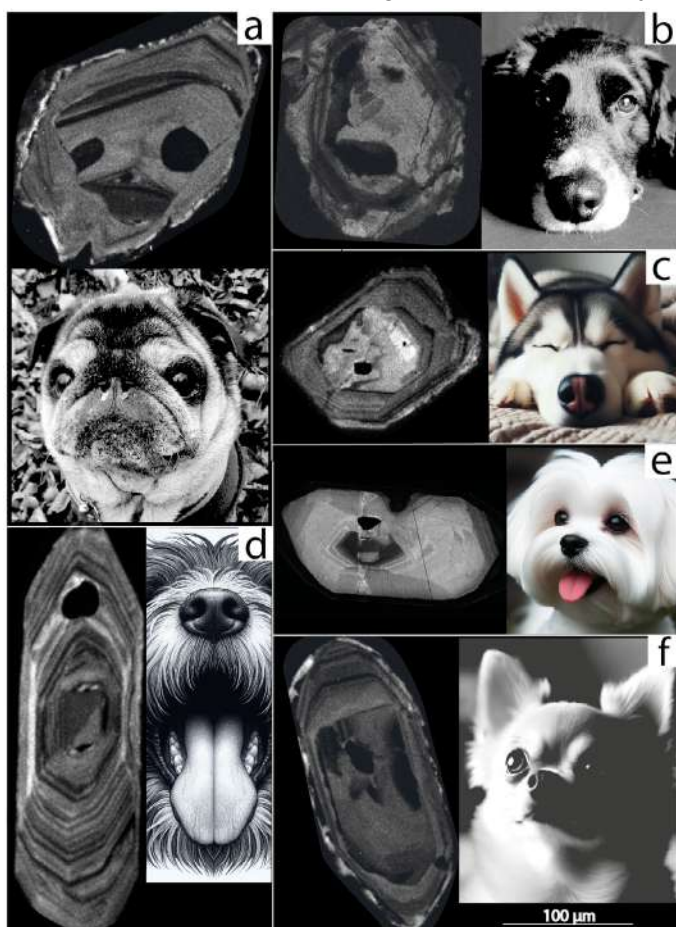


Figure 1 Comparing CL phenotypical *Zircanis* images to common sized *Canis lupus familiaris*.

Batoniite: the first “Mineral of the Year” discovered in Italy

Every year, the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC-IMA) approves about 100 new mineral species. This international group, representative of the national mineralogical societies of nearly 40 different countries, carries out the arduous task of evaluating proposals related to the nomenclature and classification of minerals, as well as assessing proposals for defining new mineral species submitted by researchers worldwide. But how does a new mineral “come to be”? First, researchers must prove, through the collection of a series of complete crystallochemical data, that the studied natural phase has a chemical composition and a crystalline structure new to science. At that point, a proposal containing all the necessary information for the evaluation of the new potential mineral species (e.g., location of discovery, description of the sample and any associated phases, physical properties, optical properties, chemical data, crystallographic data, possible relationships with other species, etc.) is drafted and submitted to the commission. The commission then assesses the validity of the reported data and gives its judgment. In the past year, five new

minerals have been described in Italy: aluminotaipingite-(CeCa), enricofrancoite, batoniite, perchiazziite, and wangkuienite. Among these, for the first time in Italy, batoniite has received the prestigious recognition of “Mineral of the Year.” This award, established in 2014 by the International Mineralogical Association, aims to highlight the work done by the CNMNC-IMA by identifying the mineral that, in the previous calendar year, stood out for its aesthetics, relevance in systematic mineralogy and more generally in Earth Sciences, exotic combination of chemical elements, and/or significance of structural configuration.

Batoniite, $[\text{Al}_8(\text{SO}_4)_5(\text{OH})_{14}(\text{H}_2\text{O})_{18}] \cdot 5\text{H}_2\text{O}$, was described by a research group coordinated by Dr. Daniela Mauro (Department of Earth Sciences at the University of Pisa and the Mineralogy Section of the Natural History Museum of the same university). This sulfate shows one of the most complex structures among minerals known so far and is characterized by the poly-oxo-cation $[\text{Al}_8(\text{OH})_{14}(\text{H}_2\text{O})_{18}]^{10+}$. This cation had previously been observed only in some synthetic phases obtained during the study of the geochemical behavior of aluminum in aqueous solution.

The studied sample comes from the abandoned antimony mine of Cetine di Cotorniano, in the province of Siena, and was studied as part of a collaboration between the Department of Earth Sciences in Pisa and enthusiasts from the Associazione Mineralogica Fiorentina (AMF) and the Associazione Mineralogica Prato e Pistoia (AMPP). The species is dedicated to Massimo Batoni, a collector from Florence, for his contributions to Italian mineralogy.

This discovery, besides teaching us more about the geochemical cycle of aluminum, one of the most abundant elements on our planet, once again illuminates the beauty of nature which, with the appropriate technological means, reveals itself in all its complexity.

The full description of the new mineral has been published in the *European Journal of Mineralogy*: Mauro, D., Biagioni, C., Sejkora, J., Dolníček, J., Škoda, R. (2023): Batoniite, $[\text{Al}_8(\text{SO}_4)_5(\text{OH})_{14}(\text{H}_2\text{O})_{18}] \cdot 5\text{H}_2\text{O}$, a new mineral with the $[\text{Al}_8(\text{OH})_{14}(\text{H}_2\text{O})_{18}]^{10+}$ polyoxocation from the Cetine di Cotorniano Mine, Tuscany, Italy.



Figure 1 Batoniite, an aggregate of white tabular crystals associated with a resinous, poorly crystalline, and unidentified Al and Fe sulfate. Photo by D. Mauro. Collection of the Museo di Storia Naturale of the University of Pisa. Photo by D. Mauro.

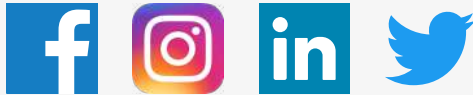
Link to the EJM article:

<https://ejm.copernicus.org/articles/35/703/2023/>

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