2 Mineralogy, Petrology and Geochemistry

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2.1 Protracted subduction of the European hyperextended margin revealed by rutile U-Pb geochronology across the Dora-Maira massif (Western Alps)

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The Dora-Maira massif is an archetypal nappe stack of subducted and exhumed upper crust. Slices of continental crust experienced metamorphism at upper blueschist to ultrahigh-pressure (UHP) eclogite-facies conditions. While the timing of peak metamorphism in the UHP unit has been extensively studied, little is known about the other units. In order to constrain the timing and conditions of high-pressure metamorphism, U-Pb-trace element analyses of rutile and titanite were carried out across the nappe stack. The data reveal Alpine peak metamorphic ages younging downwards in the stack, from ~40 to ~33 Ma. Greenschist-facies retrogression of the whole massif occurred at ~32–31 Ma, after high-pressure metamorphism of the lowermost unit (Sanfront-Pinerolo Unit). Tectonic implications include (a) continuous and fast exhumation of subducted continental crust, (b) long-lived subduction from ~π60 to ~33 Ma of the distal European margin, reconstructed to be a hyperextended margin spread over ~130 km for the Dora-Maira massif alone, and (c) the initiation of continental collision synchronous with the end of high-pressure metamorphism.
2.2
Petrochronological heterogeneities within a large pluton: from assembly to porphyry copper deposit formation

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Long magmatic histories and large volumes of magma may be key factors needed to form large porphyry copper deposits. However, the extent to which these factors, together with intrinsic parameters of the melt, might be fundamental for porphyry copper deposit formation is still highly debated. The Yerington porphyry Cu district, with its unique exposures of a tilted magmatic and hydrothermal upper crustal system (from ~ 3 to 1 kbar), has provided a natural laboratory to study different parameters important for ore formation. The composite batholith is made up of three consecutively emplaced plutons, the McLeod Hill quartz monzodiorite, the Bear quartz monzonite and the Luhr Hill granite, where mineralizing porphyry dikes were extracted from the latter.

Of the three, the McLeod quartz monzodiorite, with its volume in excess of 1000 km³, forms the main intrusion, and its zircon cargo predates mineralization in the district by 1-2 Myr. High-precision zircon petrochronology indicates a continuum in zircon crystallization ages and geochemistry from the McLeod Hill to the Luhr Hill, suggesting that the magmatic system remained active and evolving for more than 3 Myr with coeval volcanism in its early stages. Geochemical variations within the Bear and the Luhr Hill are restricted to the more evolved compositions and lower crystallization temperatures. In contrast, the zircon population of the McLeod Hill shows a protracted history of pluton assembly accompanied by notable chemical variations that can be traced in time. Trace element compositions in the zircon population of different magma batches that made up the McLeod Hill intrusion suggest that the melt from which zircons crystallized was evolving from hotter and drier magmas with little to no fertility indicators for Cu mineralization towards more evolved (wetter, cooler) and more fertile magmas over almost 2 Myr. During this timespan, reaching compositional maturation needed to form porphyry copper deposits was allowed by magma chamber growth in the upper crust through frequent magma injection from deeper in the system but without extensive volcanism.
2.3

Magmatic genesis, hydration and subduction of the eclogite-facies Allalin gabbro (Western Alps, Switzerland)

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The Allalin gabbro of the Zermatt-Saas meta-ophiolite consists of variably metamorphosed Mg to Fe-Ti gabbros, troctolites, and anorthosites which are crosscut by basaltic dykes. Field relationships of the various rock types and petrographic studies together with mineral and bulk rock chemical composition data allow the reconstruction of the complete geological history of the Allalin gabbro.

The gabbroic body intruded as a tholeiitic magma in a slow spreading MOR environment. Magmatic differentiation is recorded by clinopyroxene compositions, which show a Mg# and compatible element content decrease, and an incompatible element content increase from Mg to Fe-Ti gabbro. Exhumation to shallower depths let to subsolidus deformation and cooling of the gabbro that was followed by the intrusion of fine-grained basaltic dykes that display chilled margins. Bulk rock data of these dykes reveal strong similarities to tholeiitic pillow basalts of the Zermatt-Saas and nearby meta-ophiolites.

Subduction of the Allalin gabbro resulted in different mineral assemblages in the Mg-gabbros as a function of hydration degree. In partially hydrated metagabbros magmatic mineralogy (olivine + clinopyroxene + plagioclase) is preserved together with disequilibrium textures in the form of reaction coronae surrounding mineral boundaries. Fully hydrated metagabbros display eclogite-facies mineral assemblages, documenting the complete gabbro-eclogite transformation. Magmatic olivine is pseudomorphically replaced by omphacite + talc + chlorite + chloritoid + garnet, magmatic clinopyroxene by omphacite + garnet, and magmatic plagioclase by omphacite + zoisite + kyanite + chloritoid. The locally variable extents of hydration took place near the sea floor, as recorded by the chemical zonation patterns of metamorphic garnet coronae, the presence of Cl-apatite, and an increase in B concentrations of the pseudomorphic olivine domains.

The Allalin gabbro therefore represents a classical example of an oceanic gabbro formed in a slow spreading setting in the mid Jurassic that experienced heterogeneous hydration near the sea floor. Paleogene subduction of the gabbro to some 90 km depth produced variably equilibrated gabbroic eclogites. In eclogite-facies Mg-gabbros, the water-rich minerals chlorite, talc and chloritoid pseudomorphing magmatic olivine remained stable to these depths, revealing the potential relevance of hydrated Mg-gabbros as a fluid source at subarc depths in subduction zones.
2.4 Experimental determination of cation exchange coefficients to facilitate the prediction of Fe and Ca abundances in primary magmatic fluids

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Aqueous fluids exsolved from magmas can cause extensive alteration of the country rocks and often precipitate ore-grade accumulations of economically important metals. While the fluid-melt partitioning of ore metals between silicic melts and magmatic-hydrothermal fluids has been extensively studied, the fluid-melt exchange of major elements (Na, K, Fe, Ca, H), perhaps with the exception of Na and K, is not well understood despite the important role these elements play in controlling host rock alteration and ore metal precipitation. To bridge this gap in knowledge, a series of experiments were conducted in René41 alloy pressure vessels at 800 °C and 1750 bar to simulate conditions apparent in upper-crustal magma reservoirs. Experiments used AuAgCu-alloy capsules containing a synthetic starting glass of rhyolitic composition, a starting fluid calculated to be in equilibrium with the melt at experimental conditions and an intact quartz cylinder. The latter was thermally fractured in situ during the experiment after the attainment of equilibrium to sample the fluid phase in the form of synthetic fluid inclusions (SFI). The starting fluids were used to vary Cl content and impose variation in the aluminosity of the silicate melt through changing the amounts and ratios of chloride salts (NaCl, KCl, FeCl₂, CaCl₂) and HCl or NaOH. Run product glasses were analysed using electron probe microanalysis and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and the SFI were also analysed by using LA-ICP-MS.

Run product fluid and melt compositions were used to calculate exchange coefficients with regards to Na (K⁰⁻/Na⁻), the most abundant element in magmatic-hydrothermal fluids. All exchange coefficients show essentially no change as a function of fluid chlorinity. In the case of K-Na and Fe-Na exchange, this is consistent with previous studies (Dolejs & Zajacz, 2018; Frank et al., 2003; Holland, 1972; Student & Bodnar, 1999). The Ca-Na exchange coefficient was expected to increase with increasing Cl concentration in the fluid (Holland, 1972); however, this is not apparent likely due to the non-ideal behaviour of CaCl₂ in solution. Considering the effect of melt aluminosity, expressed here as melt ASI (molar Al / [Na + K + 2Ca]), the Ca exchange coefficient decreases (0.75 to 0.25) while the Fe exchange coefficient increases (2 to 6) in a stepwise manner just below the transition from peralkaline to metaluminous melt at an ASI of ~0.95. The value of K⁰⁻/Na⁻ further shows a sharp increase at an ASI of ~1.15, increasing from 5 to 20. The data indicate that peralkaline melts tend to release more Ca, whereas metaluminous and especially peraluminous melts release more Fe to the fluid in addition to Na and K.

Model calculations using the newly constrained exchange coefficients suggest that all fluids derived from metaluminous to slightly peraluminous melts typical for porphyry ore-forming systems will have sufficient Fe to precipitate abundant pyrite in addition to Cu-rich sulphide minerals. Therefore, the initial S/Fe ratio and average S redox state will determine if significant Au can be held dissolved in the fluid until the epithermal stage (e.g. Heinrich, 2004). Significant anhydrite precipitation without sourcing Ca from the country rock is, however, only likely from hypersaline brines, either directly exsolved from the magma or condensed during the ascent of initially low- to intermediate salinity single phase magmatic fluids.

REFERENCES
2.5
Modelling the global water cycle – the effect of Mg-sursassite and phase A on deep slab dehydration and the global subduction zone water budget

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The abundance, distribution, and transport of water between the Earth’s surface and the Earth’s interior on our planet are crucial for numerous geological, petrological and geophysical processes. Of particular importance is the role of the hydrated lithospheric mantle in cold subduction zones, where the amount of water transported into the deeper mantle is determined by the stability of the hydrous phases. These are controlled by the chemical composition, initial hydration intensity and the thermal structure of the subducting slab, as well as the thermodynamic properties of the hydrous phases in the subducting slab.

We implement different published thermodynamic data for the two dense hydrous magnesium silicates (DHMS) phase A \([\text{Mg}_7\text{Si}_2\text{O}_8(\text{OH})_6]\) and Mg-sursassite \([\text{Mg}_5\text{Al}_5\text{Si}_6\text{O}_{21}(\text{OH})_7]\) in a global set of 56 subduction zone thermal patterns (Syracuse et al., 2010) in a gridded two-dimensional thermodynamic forward model, taking the migration of fluids within the slab into account. The model uses a combination of MATLAB and Perple_X, which uses Gibbs energy minimization to calculate stable phases and amounts of coexisting fluid. This allows to quantify and benchmark the effects of different thermodynamic databases, thermal and geometric patterns of subduction zones, and chemical compositions on the water budget in the subducting slab.

Our results show that, beyond the breakdown of Lawsonite, sedimentary and mafic rocks play a minor role for the globally subducted water budget. The absolute amount of deeply subducted water in subducted ultramafic rocks as well as the different dehydration patterns and the migration of fluids within the plate strongly depends on the depth and intensity of the initial slab mantle hydration and the Clapeyron slopes of the dehydration reactions of phase-A and Mg-sursassite. The global amount of deeply subducted water for different investigated models varies between 8 x 10⁸ Tg/Ma and 1.4 x 10⁹ Tg/Ma. In subduction zones with an intermediate temperature structure, the differences span several orders of magnitude. Depending on the choice of the thermodynamic dataset the globally subducted water modelled with a 2 wt.% H₂O hydrated 12 km slab mantle is equal to subduction of the entire Earth’s surface water in 1 to 1.7 billion years.

REFERENCES
2.6 Controls on compositional zoning of zircon from the Catedral granite, Torres del Paine

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The internal zoning of crystals record the conditions of their growth, and these patterns are used to understand the evolution of the host magmatic system. However, it remains uncertain to what extent these zoning patterns are the result of equilibrium or non-equilibrium crystallisation growth processes. Understanding which of these processes dominantly controls the crystal composition is critical to our ability to accurately link textural, chemical, and isotopic data obtained from these crystals to the evolution of the wider system.

This study focusses on zircon crystals from the Catedral granite of the 12.6-12.45 Ma Torres del Paine laccolith in Patagonia, which is remarkable due to the spectacular exposure of the intrusive complex. This has allowed for detailed three-dimensional field characterisation of the architecture of the magmatic system, which comprises an early mafic feeder zone, three distinct granitic sills, and a late mafic sill complex that underlies the granitic units. Previous high-resolution U-Pb zircon geochronology places good controls on the timespans of magmatism across the entire system, with CA-ID-TIMS dates of 12.50 ± 0.01 and 12.49 ± 0.02 Ma obtained from samples of the Catedral granite (Michel et al., 2005). Here we integrate these existing geochronological and field data with textural and chemical characterisation of internal zoning of zircon crystals to constrain numerical zircon crystal growth models.

EPMA elemental mapping, NanoSIMS trace element transects, and high-resolution CL imaging of zircon from the Catedral granite reveal distinct textural populations which attest to evolving conditions over the history of the laccolith. Periodic truncation features that disrupt oscillatory growth zoning are interpreted as resorption interfaces indicating periods of zircon dissolution and growth hiatuses likely driven by an external forcing mechanism (e.g. temperature, composition, pressure). These features belie the apparently short-lived and simple crystallisation history implied by the zircon dates obtained from the Catedral granite. Intrusions interpreted to have crystallized late in the history of the Torres del Paine system contain zircons with continuous oscillatory growth zoning. NanoSIMS trace element transects reveal changes in concentration of a magnitude and wavelength that are challenging to explain via equilibrium processes. These conditions and the roles of external vs internal factors will be explored through numerical models of zircon growth from a felsic melt.

REFERENCES
2.7
Alkaline and arc-related magmas association in a subduction environment (Alexandra Volcanic Group, New Zealand): The role of melts at lithosphere-asthenosphere boundary

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Alkaline magmatism is frequently linked to intraplate settings, although it can also be observed in rift zones or in association with subduction zones. This is the case on New Zealand's North Island, where alkaline and arc-related magmas are spatially and temporally linked. This association raises questions about the mechanisms of formation of these two magma suites that are generally considered to be the outcome of distinct melting processes: “flux melting” for arc-related magmas and “decompression melting” for alkaline ones.

New Zealand's North Island constitutes the eastern border of the Australian Plate, beneath which the Pacific Plate is subducting. This Island features two distinct active volcanic zones: the Taupō Volcanic Zone in the centre, representing the current arc front associated with the subduction of the Pacific Plate; and the Auckland Volcanic Field to the northwest, which consists of an alkaline monogenetic volcanic field considered as unrelated to subduction. Nonetheless, these two types of volcanism have not always been confined to separate geographical regions. Subduction of the Pacific Plate initiated during the late Eocene period (40-30 Ma) north of the present-day Northland Peninsula. Since then, subduction has propagated southward with the resulting arc front migrating from Northland (~24-16 Ma) through the Coromandel Peninsula (~16-4 Ma) to its present location in the Taupō Volcanic Zone (2-0 Ma; Seebeck et al., 2014). During the Plio-Pleistocene (3-1.5 Ma), arc-related volcanism was active on the west coast in the Waikato region (approx. 300-400 km away from the trench). Interestingly, alkaline magmatism started during this period, in the form of a monogenetic volcanic field (Okete Volcanics) embedded within these arc-related composite volcanoes. Together, these two volcanic associations constitute the Alexandra Volcanic Group (McLeod et al., 2022). This specific intercalation suggests a petrogenetic relationship between the genesis of these two types of magma, raising questions about the processes behind the formation of alkaline melts within such a context.

The arc-related series is composed of coarse-grained to ankaramitic basalt/andesite showing high silica (46-47 wt.% for Mg#65), low titanium (0.6-1.5 wt.%), and characteristic low Nb/La ratio (< 1). In contrast, the alkaline Okete Volcanics show fine-grained olivine alkali basalt to basanite with lower silica (43-44 wt.% for Mg#65), higher titanium (1.5-2.7 wt.%), and higher Nb/La ratio (> 1). However, intermediate compositions are also observed suggesting some mixing. Geochemical modelling of peridotite melting indicates that the alkaline Okete Volcanics can result from low-degree melts produced near the garnet-spinel transition, i.e. close to the base of the lithosphere. The presence of these low-degree melts at the lithosphere-asthenosphere boundary is in agreement with geophysical studies. Melt accumulation at the base of the lithosphere is inferred in various tectonic contexts to account for seismic and electrical anomalies observed at depths of 70-100 km (e.g. Hua et al., 2023). The existence of such melts is consistent with petrological constraints if the role of volatiles in nominally anhydrous minerals is considered (Dasgupta, 2018). Trace amounts of H₂O and CO₂ lower the solidus, generating small melt fractions in the upper asthenospheric mantle without requiring any external melting factors. These parcels of melt can then migrate and accumulate at the base of the lithosphere. Geochemical modelling suggests that the chemistry and volume of the Okete alkaline magmas are consistent with the extraction of these naturally occurring low-degree melt ponding at the base of the lithosphere. We interpret the association of arc-related and alkaline magmas by the juxtaposition of two distinct mechanisms. Localised pulses of Pacific slab-derived fluids cause induce melting of the overlying mantle, generating the arc-related magmas that can either make their way to the surface or mix with some of the accumulated low-degree alkaline melt present at the lithosphere-asthenosphere boundary. We further propose that during intervals between these fluid pulses, these alkaline melts ascend to the surface using melt extraction channels created by arc-related magmas and surface faults, thus producing the Okete monogenetic volcanic field.

New Zealand's particular tectonic setting highlights the importance of melting processes in shallow environments in the production of alkaline magmas. In addition, it could explain the presence of the Auckland volcanic field further north, which is not associated with a mantle plume. In a broader context, this approach opens up new perspectives on the production of alkaline magmas in general, which are widespread in a large number of different geological contexts.
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2.8
3D melt inclusion geometries help quantify eruption triggers at Colli Albani (Italy)

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Melt inclusions, small droplets of magma trapped in phenocrysts prior to an eruption, may record volatile content of the magma before degassing, thus are a key tool for volcanologists to gain a view of the pre-eruptive state of magma. In recent years, research surrounding the feasibility of using melt inclusions for constraining true pre-eruptive volatile contents of magma has revealed the complex nature of these inclusions. Here we present 3D tomographic scans of over 2000 melt inclusions from 35 crystals from Colli Albani volcano (Italy), a low viscosity complex which makes large volume explosive eruptions. A large 3D dataset of inclusions allows for us to gain a holistic view of the evolution of a melt inclusion in the context of the mineral host (leucite versus clinopyroxene), mineral zoning, and the surrounding inclusions. We define six categories to classify melt inclusions based on shape, crystallinity, and vapour phase (glassy bubble free, glassy with a single bubble, glassy with multiple bubbles, glassy with irregular bubbles, microcrystalline, and tube shaped). This new classification allows us to make inferences about how the melt inclusion was trapped from the textural context alone. Furthermore, we investigate the validity of the often-assumed ellipsoidal shape of both melt inclusions and vapour bubbles for recalculating the volume from microscope images and find that while vapour bubbles are commonly spherical, melt inclusions are frequently irregular shapes and thus assuming an ellipsoidal shape can lead to large errors. Lastly, we use these results to investigate the saturation state of the magma of Colli Albani Volcano (Italy) prior to eruption. We find that the melt inclusions record a wide range of vapour phase fractions, suggesting that crystal growth and trapping of melt inclusions may have occurred during several phases of volatile exsolution (i.e., before and after degassing). Approximately 40% of melt inclusions with vapour bubbles have a volume fraction of >10% vapour bubble, and this can extend up to 78%. This high vapour content is indicative of a volatile enriched magma at the time of melt inclusion trapping and may reveal the trigger mechanism for the rapid ascent of the magma at Colli Albani.
2.9
The Clumped-isotope geochemistry of exhumed carbonate shear zones: Examples from the Torngat Orogen (Canada)

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Clumped isotope thermometry is a technique that ideally recovers the temperature of carbonate formation without any assumptions regarding the composition of precipitating water and/or oxygen isotope composition of another mineral phase, such as required for conventional stable isotope thermometry. However, applications of this technique to high-grade metamorphic marbles remain limited. Here, we present clumped- (Δ47), stable O and C isotope compositions measured across sheared high-grade marbles from the Torngat orogen, Canada, to explore the role of retrograde metamorphic reactions and deformation on Δ47 values. The petrography shows that shear zones are associated with local dissolution of carbonate grains and the appearance of retrograde minerals. Both metamorphic assemblages and C-isotope equilibrium between carbonate and graphite support that the shear zones formed from peak-temperature conditions and during retrograde conditions at temperatures in the range 550-590 °C. Clumped isotope compositions of the host dolomitic marbles record apparent peak metamorphic equilibrium temperatures of 300-500°C. Although these temperatures are significantly lower compared to regional peak temperatures derived from metamorphic reactions (about 750 °C), and C-isotope equilibrium between carbonate and graphite (about 730 °C), they are higher than other apparent Δ47 temperatures of dolomitic marbles elsewhere (e.g., metamorphic core-complex of Naxos, Notch Peak aureole). In calcitic marbles, temperatures recorded by Δ47 are between 151 °C and 260 °C, consistent with apparent temperature measured in other calcitic marbles. Within the shear zone, measured Δ47 temperatures along the shear zones are inconsistent, giving very low values (even lower than 0 °C). Our results suggest that Δ47 does not record the absolute peak temperature experienced by marbles. However, the abrupt changes in Δ47 values across the shear zone suggest Δ47 disequilibrium during CO2-rich aqueous fluid-rock interactions.
2.10
An astonishing choice: First petrological examination of Neolithic axe heads from Düdingen, Fribourg

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Switzerland possesses a rich catalogue of Neolithic archaeological sites that have been extensively excavated and documented by cantonal services and universities. Among the most important artefacts of this time are axeheads, carved from various crystalline rocks, which were used both as ordinary tools and as representative objects for high-ranking members of these past societies. Especially from the 6th to the 3rd millennium BC, findings of green axeheads made from eclogites and jadeitites from Alpine sources appear in archaeological sites all over Europe, indicating that trade and exchange networks over thousands of kilometres were already in place at the time. In addition to the study of production techniques, it is especially the potential of tracing these artefacts along sites that defines their invaluable scientific value. However, the petrographic study of the artefacts has long been restricted to non-invasive, macroscopic examination. Fortunately, a recent change in conservation policies of several collections now permits the application of classical petrographic methods that provide much more detailed insights into the materials that were chosen by the artisans. For this first pilot study, a total of 17 samples of broken axeheads and percussive tools from the site of Düdingen-Schiffenengraben (ca. 4000 BC), Canton of Fribourg, were analysed. The results show that a large part of the sampled axeheads were made from surprisingly unusual and rare rocks, such as epidotitites showing complex corona textures around garnet. Percussive tools, macroscopically resembling normal coarse-grained gabbros, turned out to be completely transformed, leaving unique pseudomorph structures. None of those rocks have been mentioned in previous literature yet and their unique composition indicates a specific material choice that cannot be explained by simple collection of river gravel around the site. While making the samples difficult to study and define, the unusual nature of these rocks is a promising indicator for future provenance attempts, given the proposed scarcity of the observed rock types in the field. This paper aims to showcase the potential of classical petrography applied on Neolithic artefacts which, while being invasive, adds a whole array of new data that can be used to better understand interconnectedness of early societies. It also counts on the support of the petrological community, whose expertise is crucial to trace potential primary sources of the raw material encountered in the archaeological record and refine the reconstruction of Neolithic exchange networks all over the European continent.
2.11
A general approach to quantify phase equilibria and silicate mineral stability fields in calc-alkaline basaltic systems

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As the “in-situ” study of magmatic processes is only possible to a very limited extent at some active volcanoes, igneous petrology predominantly relies on the analysis and interpretation of solidified magmatic products and their crystal cargo. As a consequence, a huge variety of petrological tools has been developed over the last years that have been widely applied to igneous rocks to reconstruct magmatic processes (e.g. thermobarometers or crystallisation algorithms like rhyolite-MELTS and COMAGMAT). However, most thermobarometers are frequently of only limited validity due to significant uncertainties and model interdependencies, while thermodynamic models suffer from severe limitations (especially for H₂O-bearing systems) complicating the application of these tools to natural rocks.

The prediction of phase equilibria is particularly complex for calc-alkaline systems, because water and oxygen fugacity vary over wide ranges. This study is an attempt to fill this gap by providing new experimental data exploring systematically the effects of temperature, pressure, magma composition, H₂O, and fO₂ on phase equilibria in calc-alkaline basaltic systems. Our experimental program was designed to extend existing high-pressure experimental datasets (400-900 MPa) on a high-Mg basalt from the Adamello Batholith (Italy) and a high-Al basalt from the Cascades (U.S.) to upper crustal pressures. Experiments were run in internally heated pressure vessels (IHPV) at 200 and 400 MPa and varying H₂O contents (0-9 wt.%) with fO₂ conditions buffered between NNO-1 and NNO+2.3. Additional experiments at 500 MPa were performed on a high-Mg basalt from Klyuchevskoy volcano in Kamchatka (Russia) to extend the range of investigated starting material compositions and pressures.

Beside changes in mineral assemblages, we established the influence of different crystallisation parameters on silicate mineral chemistry (e.g. for olivine, clinopyroxene, and plagioclase). We combined our new data with high-quality experimental data from literature to formulate empirical mineral saturation models for plagioclase and clinopyroxene predicting the saturation of these phases as a function of bulk system composition, pressure, temperature, H₂O, and fO₂. Furthermore, employing our experimental data compilation, we tested existing mineral-based thermobarometers to provide some general insight on their limitations and present some recommendations for their application to natural rocks.
2.12

Redox state, sulfur and chalcophile element budgets during magma differentiation in thick continental crust: a case study on the Parinacota volcano

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Porphyry-type ore deposits form via metal sulfide precipitation from magma-derived fluids at convergent plate boundaries. The potential of a magma to generate porphyry ores depends on the availability of volatile elements and ore metals, as well as the apparent redox conditions throughout the course of magma differentiation. The redox state of the magma controls magmatic sulfide stability and therefore chalcophile metals sequestration and potential re-mobilization. Furthermore, it controls the speciation of sulfur in the magmatic volatile phase and thus the temperature range and spatial focusing of sulfide precipitation in the associated hydrothermal system. The evolution of volatile element and chalcophile metal budgets during magma differentiation in continental arcs is still a matter for scientific debate.

To address this problematic, we studied the Parinacota volcano in the Central Volcanic Zone of the Andes, which is characterized by particularly large crustal thickness (up to 70 km). We used silicate melt inclusions (SMI) from all major eruptive units to decipher chalcophile metal, volatile and redox systematics as a function of pre-eruptive magma storage depth and degree of differentiation. The combination of SMI data with mineral textures, phase equilibrium constraints and geothermobarometric calculations allowed the identification of at least three distinct components within four separate magma storage zones. Magmas at Parinacota are invariably oxidized, and notably the most primitive basaltic to basaltic andesitic magmas have the highest oxidation state. In addition, the most primitive melts have the highest Sr/Y ratios and also display highly elevated sulfur concentrations reaching up to about 7000 ppm, well above typical arc magma values (500 – 2500 ppm). These findings suggest that the high oxidation state of the magmas at Parinacota is imposed in the mantle source by the influx of slab derived fluids, or with a smaller likelihood, during very early stages of magma differentiation in the mid- to lower crust. Positive correlations between Sr/Y and S, as well as Sr and Ba indicate that Sr, S and Ba are donated by slab-derived fluids along with other fluid mobile elements, and that extensive magma differentiation at deep crustal levels is not always a prerequisite for the generation of high-Sr/Y, S and Cl-rich chalcophile metal-bearing fertile magmas.

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2.13
Fluid-mineral equilibrium under stress investigated through molecular dynamics

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The interpretation of phase equilibria and reactions in geological materials relies on standard thermodynamics. This thermodynamics assumes that the stress in the systems is hydrostatic and homogeneous, which means it is the same for all the phases involved. However, stress gradients and non-hydrostatic stresses are typical in rocks. Even in porous rocks with fluids, non-hydrostatic stress can arise in the solid matrix because the solid grains are in contact with the fluid and with other grains with varying contact areas. Such a condition casts doubts on the predictive power and accuracy of existing hydrostatic multiphase thermodynamic models. However, there is still no accepted theory to evaluate the thermodynamic effect of non-hydrostatic stress on reactions (e.g. Hobbs & Ord, 2015; Tajčmanová et al., 2015; Wheeler, 2014).

We have investigated the direct effect of a homogeneous non-hydrostatic stress on the solid-fluid equilibrium with molecular dynamics simulations (Mazzucchelli et al., submitted). With such simulations the energy of the system, the pressure of the fluid, the stress of the solid, as well as the overall melting and crystallization process can be monitored until the stressed system reaches the equilibrium conditions. Our results show that for simple systems at the stress range expected in the lithosphere, the shift of the pressure of the fluid-solid equilibrium is small, consistent with theoretical predictions (Frolov & Mishin, 2010). On the contrary, the mean stress of the solid is significantly affected by the applied non-hydrostatic stress and can deviate substantially from the pressure of the fluid. In the presence of large non-hydrostatic stresses, the stressed system becomes unstable and a rim of hydrostatically-stressed solid eventually crystallizes around the initial high-stressed solid core. The overall differential stress of the solid phase decreases while preserving the total stress balance, until the solid-fluid system reaches a new stable equilibrium. These results suggest that phase equilibria can be accurately predicted by taking the fluid pressure as a proxy of the equilibration pressure. Moreover, models used to describe equilibria and reactions in minerals and rocks under stress should not use the pressure of the fluid as a proxy of the mean stress of the solid, and should therefore not equate the thermodynamic pressure of the reaction to the mean stress of the solid.

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2.14
Sulfur enrichment on the surface of Mercury

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The NASA MESSENGER probe to Mercury observed unexpectedly high abundances of S on the surface of the planet (Nittler et al. 2011; Weider et al. 2015). The observations suggest that sulfides on Mercury’s surface include CaS (oldhamite) and MgS (niningerite), at extremely reducing conditions, several log\(fO_2\) units below the Iron-Wüstite buffer (IW), at IW-5 to IW-7 (Zolotov 2011; Namur et al. 2016). We propose that these sulfides are not magmatic phases, but formed by sulfidation of silicates with S-rich volcanic or fumarolic gases (Renggli et al. 2022). For example, diopside reacts with CS\(_2\) to form CaS, MgS, and quartz:

Here, we present mid-infrared spectral observations of experimentally sulfidized silicates, which will allow us to directly test the sulfidation hypothesis. The Mercury Radiometer and Thermal Infrared Spectrometer (MERTIS) onboard ESA/JAXA BepiColombo mission to Mercury will map the planet’s surface in the mid-IR (Hiesinger et al. 2022). We conducted the experiments in sealed and evacuated silica glass ampules at temperatures from 800 to 1200 °C. Experimental run products were measured by micro FTIR with a Bruker Hyperion 3000 using a MCT detector. We report observations over the spectral range from 800-1300 cm\(^{-1}\) at a spectral resolution of 2 cm\(^{-1}\).

The silicated minerals reacted with the reduced S-rich gas to form the Ca- and Mg-rich sulfides and quartz, as predicted by the chemical reaction above. The extent of sulfidation of the silicates depends on reaction temperature, reflected in the mid-IR spectra. We do not observe sulfide features in the FTIR spectra. However, the sulfidation reaction is identified by the formation of quartz, with strong shifts in the spectral features.

In summary, we argue that on Mercury, reduced S-rich fumarolic and volcanic gases rapidly react with silicate minerals and glasses to enrich the surface in S by generating sulfides and quartz. According to MESSENGER data, quartz is not expected to be present in the most Mercury terranes (Namur & Charlier, 2017). Therefore, BepiColombo’s finding of quartz with the MERTIS instrument in areas with significant S enrichment, would be consistent with our theory that Mercury’s surface silicates have undergone sulfidation. Importantly, less reducing conditions would be needed for the surface basalts if the sulfides are not magmatic phases. Sulfidation of silicates at the planet’s surface would follow substantial S degassing as a result of oxidation of melts from IW-7 to IW3 from the mantle source to the surface of Mercury.

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2.15 Tracking fluid sources in the slab: Evidence from HP metabasalts from the Tianshan, NW China

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Slab fluids, which are released by the subducting oceanic lithosphere through compaction and dehydration processes, migrate within the slab upwards to the slab-mantle wedge interface. With that they represent an essential mechanism for the transfer of volatiles from the slab to the mantle wedge. Consequently, hydrophile volatiles can be used as tracers to determine intra-slab fluid flow processes. However, migration processes of slab dehydration fluids, particularly with regards to transport mechanism of redox sensitive elements like sulfur, as well as the evolution of fluid sources during metamorphism of the slab, are not yet understood well.

In this study we investigate an eclogite-facies metabasalt from the HP/LT Akeyazi Metamorphic Complex of the South Tianshan Orogen, NW China. The sample comprises several omphacite-dominated HP veins that crosscut the blueschist-dominated matrix and formed under peak metamorphic conditions. Using mineral chemical analyses combined with in situ δ34S measurements of pyrite, as well as trace element and isotope analyses of C, Sr and Pb in mineral and vein separates, we track fluid sources and the transfer of the redox sensitive elements S and C and reconstruct the metamorphic evolution and the related intra-slab fluid flow of the studied sample.

All isotope systems provide evidence for multiple episodes of fluid-rock interaction with fluids derived from distinct sources. In particular, pyrite grains show patterns in in situ δ34S values which record changes in fluid chemistry that are supported by Sr isotope and trace element compositions. Large pyrite grains recording microbiially derived S reveal low temperature seafloor alteration affecting the protolith pillow basalt prior to subduction. This is supported by dolomite δ13C values close to seawater-carbonate compositions. Based on chemical variations, the rock was infiltrated by a two stage intra-slab fluid-flow under peak to prograde metamorphic conditions during ongoing subduction, responsible for the formation of the omphacite-dominated HP-veins. MORB-like pyrite δ34S signatures of around -0.75‰ as well as Sr-mixing lines between AOC and slightly altered basalt indicate that the first HP fluid originated from dehydrating ocean floor basalts. In contrast, negative pyrite δ34S values of around -10.75‰ and Sr signatures correlating with the mixing of altered basalt with seawater454Ma and pelagic clays suggest that the second HP fluid originated from the basalt-seafloor sediment transition. Pathways formed by the first fluid were reused and enlarged by the second fluid, which however also formed new pathways. This sample provides detailed insights into intra-slab fluid flow and fluid-rock interaction processes at HP/LT metamorphic conditions and allows a better understanding of fluid transfer and changes in fluid sources during subduction zone processes.
2.16
The gold endowment of alkaline melts: Insights from LA-ICP-MS analysis of silicate melt inclusions

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Alkaline magmatism can generate giant epithermal Au deposits (Jensen & Barton 2000). Prominent examples of this economically significant mineralization style are Ladolam (Papua New Guinea) and Cripple Creek (Colorado). The root causes determining ore fertility of alkaline melts remain enigmatic. Silicate melt inclusions (SMI) that entrapped primitive melts can be used to trace magma evolution and changes in ore-relevant element concentrations. Since alkaline melts are typically assumed to represent small magma volumes produced by low-degree partial melting, their Au content may be decisive for the formation of giant Au deposits such as Ladolam on Lihir Island (>1500 t of Au, Müller et al. 2001). We reconstructed the magmatic evolution of Lihir Island, Papua New Guinea, using SMIs, mineral geochemistry and oxythermobarometry calculations to identify key parameters that influence ore fertility and report the first Au concentrations for alkaline melts determined in-situ by LA-ICP-MS analysis of SMIs.

Our results indicate that alkaline melts evolved from ankaramitic (CaO/Al₂O₃ > 1, MgO > 8 wt.%) parental magmas. Experimental studies suggest that ankaramitic melt can be generated by high-degree partial melting of a clinopyroxene-rich source (Médard et al. 2006). Enrichment of fluid-mobile and depletion of fluid-immobile trace elements in SMIs indicate that the source lithology was metasomatically overprinted, in agreement with reported metasomatized mantle xenoliths found near Lihir Island (McInnes et al. 2001). Initial melts were highly oxidized (ΔFMQ +4), relatively dry (≤ 0.5wt.% H₂O), and metal-rich (~ 100 μg/g Cu). Sulfur and Cl concentrations in contrast are not particularly elevated. With subsequent crystal fractionation, dominated by clinopyroxene crystallization, alkali metal concentrations increased rapidly, producing the alkaline character of the melts. Similarly, water, volatile and metal concentrations also increased. A rapid decrease in S contents of SMIs with continuous fractionation was caused by exsolution of a low-density single-phase fluid, which is recorded by the presence of small vapor-rich fluid inclusions co-existing with SMIs.

Gold concentrations in SMI are variable but generally high (~ 1 to 100 ng/g) compared to typical calc-alkaline arc magmas (<5 ng/g, Grondahl & Zajacz 2022). However, Au concentrations are not correlated with any other analysed element concentrations and are often recorded in time-integrated LA-ICP-MS signals as high-intensity single readings (i.e., "spikes"). The systematic association of these high Au intensity anomalies with the transient SMI signals indicates that these high Au intensities might be caused by ablation of nanometer-sized Au particles hosted in the SMIs. These Au nanoparticles may be inherited from the metasomatized cumulate source lithology and play an important role in the fertility of these melts for gold mineralization.

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2.17
Different formation processes for metamorphic olivine in Erro Tobbio unit, Italy

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The high-pressure antigorite-serpentinites from the Erro-Tobbio Massif (Italy) contain metamorphic olivine that is thought to have been produced by the antigorite + brucite dehydration reaction. However, the Erro-Tobbio Massif also contains subducted peridotites that are only partially serpentinized, and metamorphic olivine could also have been formed by recrystallization of relic mantle olivine (Scambelluri et al., 1991).

In this study we investigate the olivine formation process using in situ oxygen isotopes and trace elements (SIMS and LA-ICP-MS, respectively) in metamorphic olivine.

Among five olivine-bearing samples, ranging from static olivine to olivine in shear bands, fracture networks and veins, we found two distinct types of metamorphic olivine:

1. Olivine, that appears as porphyroblasts or as static olivine, overgrown by antigorite shards, has low Li, low B, relatively high Ni/Mn ratio and $\delta^{18}O$ values of ~5–5.5 ‰;
2. Olivine in shear bands, fracture networks and veins has variable Li, high B but low Ni/Mn, $\delta^{18}O$ values of ~4–5 ‰ and is in isotopic equilibrium with the antigorite.

The low Li and B olivine (i) overlaps with the composition of mantle olivine from the partially serpentinized peridotites of the Erro-Tobbio unit and has a Ni/Mn ratio that partially overlaps with the Ni/Mn ratio of mantle olivine. However, the high MnO content of 0.3–0.4 wt.% indicates that olivine (i) is metamorphic. We propose that this olivine is the product of recrystallization during subduction of relic mantle olivine (Ol_rec), in contrast to olivine (ii), which is the product of the antigorite + brucite dehydration reaction (Oldehyd). The results demonstrate that both types of metamorphic olivine, formed by different processes, can occur together within single samples of the same unit.

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2.18
Preserved conditions of oceanic serpentinization in a subducted slice of lithospheric mantle

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Serpentinization of ultramafic rocks and their recycling in the mantle via subduction is a major contributor to the element cycling in the Earth’s interior, from the element uptake in the oceanic environment to the dehydration of serpentinites in subduction zones. The Erro-Tobbio Massif (Western Ligurian Alps) represents a slice of fossil oceanic lithosphere that was serpentinized during the opening of the Tethyan ocean in the late Jurassic and was later subducted to high-pressure conditions during the Alpine collision. We studied samples that preserve evidence of lizardite formation during shallow low-temperature hydration in the oceanic environment as well as samples that contain antigorite that formed during subduction after the lizardite-to-antigorite transition. The aim is to compare the isotopic and chemical characteristics achieved at the different conditions of serpentinization and to assess the extent of homogenization during metamorphism.

The oxygen isotopic composition of serpentine (analyzed in situ by SIMS) is used to constrain the temperature of hydration, while the trace element composition (measured by LA-ICP-MS) serves to estimate the fluid composition during hydration. Transition metals (Ni, Cr, V, Co, Sc, Mn, Zn) are immobile elements and their concentrations in serpentine should be indicative of the primary mantle minerals that serpentine has replaced. In the oceanic serpentinite samples, the transition metal compositions of lizardite remain distinct in the olivine and pyroxene sites. Antigorite can preserve a similar transition metal composition to the mantle mineral it replaces, but it can also exhibit a range of transition metal compositions between the olivine and orthopyroxene poles. This suggests that the lizardite-to-antigorite transition partly redistributes the trace element composition. Lizardite in oceanic serpentinite samples shows significant variations in δ18O, indicating a temperature range of 70-325°C during serpentinization considering seawater as fluid, but higher temperatures could be calculated for a hydrothermally evolved fluid. Conversely, antigorite shows a narrow range of δ18O values (5.4–7.5‰). During low-temperature hydration, the fluid-mobile elements (Cl, B, Li, Sr) are sourced from the seawater and incorporated into serpentine. In particular, the Cl/B ratio can increase among the different lizardite textures during oceanic serpentinization, indicating a more saline fluid resulting from fluid-rock interaction. Antigorite is generally depleted in Cl and B compared to lizardite, likely due to the loss of fluid-mobile elements during the lizardite-to-antigorite transition.

The geochemical variability of lizardite suggests that it formed under varying temperature and water-rock ratio conditions during hydration in oceanic environments. This study demonstrates that the metastable oceanic serpentinization can persist during subduction. Furthermore, the Erro-Tobbio antigorite serpentinites reveal the homogenization of the major elements (especially oxygen), but the trace elements are either released to fluids (e.g., fluid-mobile elements) or distributed between olivine and orthopyroxene sites (e.g., transition metals). This implies that the fluid resulting from the antigorite-out dehydration reaction has a constant and defined composition with respect to the major element (especially δ18O), regardless of the hydration processes in the oceanic environment, while the trace element composition is more influenced by hydration and dehydration processes.
P 2.1
Lithostratigraphic characterisation of the Paleozoic units of the Suretta Nappe, Eastern Swiss Alps: insights from U-Pb dating of zircons and geological mapping in Val Madris (Grisons)

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We present a new lithostratigraphy of the Paleozoic units of the Suretta nappe based on field mapping and U-Pb dating of detrital zircons and of garnets in metasediments.

The Suretta nappe is part of the middle Penninic nappes in eastern Switzerland and consists of polymetamorphic basement rocks, Permian intrusions in the northern part and a Permo-Mesozoic cover (Scheiber et al., 2013).

In recent literature, a paleozoic metasedimentary unit has been mapped between an older basement and the Permo-Mesozoic cover. This unit has been referred to as “Permian”, “Late Palaeozoic” or “monocyclic unit” (Baudin et al., 1995). It has only been poorly defined and not yet dated.

To refine the lithostratigraphy and the evolution of the Suretta nappe, geological mapping in Val Madris, petrographic descriptions, whole-rock geochemical investigations, and uranium-lead (U-Pb) detrital zircon and garnet geochronology have been performed.

This study shows that we can distinguish two metasedimentary formations between the older basement and the Permo-Mesozoic cover. The new ages prove that the stratigraphically lower Valle di Lei Formation is pre-Permian. The upper Val Saenta Formation contains Permian detrital zircons and is probably late Permian (Figure 1). The Val Saenta Formation can be correlated with the Col de Chassoure Formation in the middle Penninic Mont Fort and Siviez-Mischabel nappes in the Western Alps (Sartori et al. 2006).

Figure 1. Our new geological map of the Val Madris with the dated samples.
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P 2.2
Distribution of C-bearing phases in the Ivrea lower continental crust (Ossola Valley, Italy)

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The Ivrea lower continental crust consists of underplated mafic as well as metasedimentary rocks. In the metasedimentary rocks, carbon in the form of residual carbonates and graphite can potentially be stored for millions to billions of years. Yet, the abundance of the carbon-bearing minerals is poorly quantified.

Rock samples from the Ossola valley collected from outcrops as well as drill cores obtained from the DIVE-project were studied regarding the distribution of C-bearing phases in the upper section of the lower continental crust. The drill core samples are mainly biotite schists (Qtz + Pl + Bt ± Grt ± Sil ± Kfs), amphibolites (Amp + Pl + Qtz ± Px ± Bt) and calcsilicates (Qtz + Pl + Grt + Px + Ttn ± Amp). Complementary marbles (Cb + Qtz + Px + Ttn + sulfides) and higher-grade metasediments (stronalites) were collected at outcrops. In most lithologies, varying degrees of partial melting has been observed. Graphite occurs in the matrix of biotite schists and as inclusions in garnet. Moreover, carbonates are present in relatively pure marble lenses and as interstitial grains in calcsilicates and to a lesser extent in amphibolites.

Total carbon analysis (TIC/TOC) revealed that the biotite schists contain between 0.01 and 1.21 wt.-% carbon whereas in case of amphibolites and calcsilicates, values range from 0.01 to 2.42 wt.-%. Furthermore, elemental carbon is dominant in the biotite schists whereas amphibolites and calcsilicates contain higher amounts of inorganic carbon.

An attempt to use apatite as a monitor for carbon mobilisation by quantification of the CO₂ content via ATR-FTIR (according to the method of Hämmerli et al., 2021) revealed that the mineral is CO₂-free in all rock types. This implies that apatite is either not a suitable monitor for carbon mobility in the investigated rocks or that mobilisation did not take place in the studied areas.

Garnets in C-bearing samples show compositional differences depending on the hosting lithology. The prevailing type of garnet in the biotite schist is composed of Alm₆₅Grs₁₁Prp₈Sps₈Adr₂. The Fe-component is lower and the Ca-component higher in the amphibolite (Alm₆₂Grs₁₅Prp₁₅Sps₅Adr₃). In calcsilicate rocks, this trend is even stronger, resulting in a composition of Alm₅₄Grs₂₉Prp₆Sps₉Adr₃. Therefore, garnet compositions can be used to distinguish between carbonate-rich protoliths for calcsilicates and carbonate-poor protoliths in case of the amphibolites.

Our study shows that felsic lithologies of the metasedimentary lower crust contain up to 2.42 wt.-% C and thus represent a reservoir that should be considered in the carbon budget of the crust.

REFERENCES
P 2.3
A multi-method approach to investigate pluton formation and melt production in the deep crust: case study of the El Oro Complex in Ecuador

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The El Oro Complex, in the southwestern part of Ecuador, is a tilted crustal section of metasediments from the Ecuadorian forearc. The lower segment of this complex underwent partial melting triggered by the intrusion of gabbroic magma over a relatively short period of 5 million years during the Triassic era. This event led to the formation of an S-type pluton known as the Marcabelí granitoid. Such a short-lived episode provides an excellent opportunity to gain a better understanding of the mechanisms underlying the formation and transport of melt in the continental crust, spanning deep to shallow regions.

We present a thermal model coupled with thermodynamics to simulate partial melting and melt extraction for different scenarios during the Triassic metamorphic history of the El Oro Complex. Temperature and assemblages are simulated at each timestep and melt is extracted from the model using a liquid percolation threshold. The findings of our simulations are compared with new field, geochemical and geochronological data. U-Pb geochronology and trace element compositions were performed on zircons from the granitoid and its source, allowing to have better constraints on the history and duration of the pluton emplacement. Combining these different approaches provide new insights into the melting processes of the deep continental crust.

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P 2.4
Thermodynamic calculations of fluids in the deep crust

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During orogenesis, metamorphic rocks devolatilise as they are subjected to an increase in Pressure and Temperature. The produced fluids exert a first-order control on metamorphic mineral assemblage development and enable mass transfer within the crust. Therefore, quantifying the chemical composition of fluids released by different rock types and lithologies at a range of Pressure-Temperature conditions is critical.

Current thermodynamic models simplify metamorphic fluids to three or fewer of their main components: H₂O, nonpolar gases, salts, and host-rock oxide components. We compare aqueous speciation calculations from different programs that use different models to investigate the effect on crustal mass transfer calculations. The dissolution of rock-forming minerals into aqueous species within a fluid is primarily determined by a fluid’s density, dielectric constant, and chlorinity. Therefore, we examine how the thermodynamic properties of aqueous species vary due to different equations of state for H₂O, different electrostatic models, and different chlorinity values. The results of this study have wide-ranging implications for the thermodynamic modelling of complex crustal fluids.

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P 2.5
Numerical simulations of gold deposition by boiling in epithermal systems

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Low-sulfidation epithermal deposits are an important source for gold and silver worldwide. They usually form in volcanic provinces in shallow crustal depths at temperatures between ~150 and 300°C. It is widely accepted that active geothermal systems are present-day analogues of systems which formed low-sulfidation epithermal deposits in the past. Previous studies on both active geothermal and fossil epithermal systems have revealed key aspects of low-sulfidation epithermal ore formation, e.g., that boiling is a main mechanism for high-grade gold precipitation (Simmons et al., 2005).

However, epithermal systems are characterized by a complex interplay between hydrological, geological, chemical, and physical processes, and key questions concerning the formation of economic gold deposits have not been answered yet. Especially, it is unclear how they have to interact such that boiling zones can efficiently form economic gold deposits. This question is of pivotal importance since many geothermal systems lack economic gold mineralization, as evidenced by active systems – there is no present-day geothermal area where active ore deposition has been recognized (Hedenquist & Lowenstern, 1994).

Computer simulations are a powerful tool to simulate deterministic systems showing complex emergent behaviour, as it is the case for geothermal systems (Ingebritsen et al., 2010). Assumptions based on field observations can be included as boundary conditions or input parameters and the behaviour of the system as a response to changes in these conditions can be investigated. Despite the great potential of numerical approaches, only some partial problems concerning the ore formation in epithermal systems have been modelled so far.

We perform 2D fluid flow simulations in a magmatic setting with a cooling pluton in the subsurface. The porous-media flow simulations are carried out using the modelling platform CSMP++ and coupled with a reactive-transport model for gold transport and precipitation in the crust, focusing on key aspects controlling gold solubility, mainly H₂S partitioning between the water vapor and liquid phase during boiling (Drummond & Ohmoto, 1985). The main focus of our study is (1) to investigate the role of host rock permeability on the distribution of gold precipitates in the system and (2) to estimate maximal gold grades that can ideally be achieved in a porous-media setting without fractures or other highly-permeable pathways focussing fluid flow.

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P 2.6
Volatile budgets and evolution in porphyry-related magma systems, determined using apatite

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To what extent is the volatile evolution of mineralising systems, such as porphyry ore deposits, representative of volcanic plumbing systems? To answer this key question, melt and fluid inclusion compositions are commonly probed to constrain the volatile evolution near the magmatic-hydrothermal transition, as they capture a direct record of the dissolved or exsolved volatile phase. However, fluid inclusions are scarce, challenging to analyse, and melt inclusions may be affected by post-entrapment re-equilibration processes. We propose that in-situ analysis of apatite, which incorporates volatiles in its crystal lattice, may offer a superior alternative to melt and fluid inclusion analysis.

We use apatite as a recorder of the volatile budget of magmas and derive the volatile saturation state of magmatic systems. We model the volatiles in apatite following (Humphreys et al. 2021) but with the improvement that we integrate the temperature-dependent exchange coefficients that reflect the non-ideal mixing of F-Cl-OH in apatite (Li & Costa 2020). We model the apatite dataset of the Corrocohuayco porphyry-skarn Cu deposit, Peru (Chelle-Michou & Chiaradia 2017) which comprises early gabbrodiorites, mineralised hornblende-biotite porphyries, and later rhyodacite dykes. The modelling determines initial F, Cl and H2O of each magma and allows us to estimate the timing of volatile saturation relative to crystal fractionation. Further, we are able to retrieve both the melt and fluid compositions (e.g., salinity) at the point of volatile saturation. Our modelling results fall within the range of direct measurements of melt and fluid compositions. This provides a new way to determine whether there are fundamental differences in magma crystallisation and fluid evolution in barren and mineralised systems.

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P 2.7
Intra-Grain Variability of Trace Elements in Rutile

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Rutile is one of the main accessory minerals in high grade metamorphic rocks and is frequently used as petrogenetic indicator mineral. Zr-in-rutile thermometry, U-Pb geochronology, and discrimination diagrams based on various trace elements are often used to infer formation processes of metamorphic host rocks or protoliths of detrital grains. Homogeneity of trace elements is often implicitly assumed. However, it has been shown that Zr-, Nb-, and Ta contents in rutile can vary from core to rim, but systematic studies of inter grain variability of trace elements in rutile are lacking.

We will present results from laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) mapping on rutile grains from low-T – high-P metamorphic rocks, hydrothermal clefts, and pegmatites. Maps have been acquired by line scanning with spot sizes of 12–38 μm, depending on grain size, resulting in a spatial resolution of up to 12 μm. Data reduction was performed using the software XMapTools.

All samples are zoned in one or more trace elements, showing several different zoning patterns. Hydrothermal and pegmatitic rutile show predominantly sector zoning. Oscillatory trace element zoning within a sector are interpreted to indicate variability in fluid composition during rutile growth within these samples. Rutile from quartz veins in low-T eclogites show decreasing zirconium content from core to rim which is consistent with rutile growth during retrograde vein formation. Calculated Zr-in-rutile temperatures are in the range ~450–550 °C and decrease by ~20–30 °C from core to rim. Thus, Zr-in-rutile thermometry might be reliably applied in such cases. Contrarily, low-T metamorphic rutile shows irregular zoning patterns in Zr. This suggests that Zr contents depend on Zr activity or were modified by sample internal fractionation during rutile growth, rather than reflecting temperature variations. This result indicates that Zr-in-rutile temperatures should be used with caution to constrain the metamorphic evolution of low temperature rocks. Additionally, Nb and Ta are only partially correlated within a single grain, and Nb/Ta-ratios vary significantly between growth zones. Two processes can explain these variations (1) Nb and Ta fractionation during rutile growth, and (2) later modification during post-growth recrystallisation.

Rutile trace element contents have high intra-grain variabilities, with different behaviour depending on, lithology, P–T-conditions, or fluid availability. This has significant implications for using rutile as petrogenetic indicator mineral. Further investigation into understanding the processes responsible for observed trace element zoning are required.
P 2.8
Modelling fluid recycling and fluid fluxes during subduction

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Dissolution of hydrous minerals during prograde metamorphism, which releases aqueous fluids, is thought to play an important role in triggering subduction-related processes such as earthquakes or partial melting. Petrological models can simulate the release of metamorphic fluids by hydrated lithologies, and are used in this study to understand the fate of these fluids. An advanced petrological model based on Gibbs energy minimization was developed to simulate the fluid production and associated fluid fluxes in a multi-rock system during prograde metamorphism. Two scenarios are tested with (1) a fully hydrated mafic layer at the bottom of a stack of partly hydrated mafics and (2) a stack of mafics alternating between hydrated and partly hydrated material. Hydrated mafic lithologies typically lead to continuous fluid release due to the mineral decomposition. Relatively dry lithologies thus have the potential to consume such released fluids assuming pervasively infiltration. This internal fluid recycling may stabilize hydrous phases under blueschist to eclogite facies conditions and influence the fluid accumulation, migration and release from the subducted stack. As a consequence, the effective fluid release from the stack can be delayed by >10 km. We propose that this process results in the recycling of released fluids within the slab and might explain localized fluid releases in subduction zones, which are i.e. required to contribute to partial melting of the mantle wedge.

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P 2.9
P-T conditions and timing of melting in the Ivrea lower continental crust

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Partial melting plays a fundamental role in a wide range of geological processes including the formation and modification of the continental crust. In particular, the chemical differentiation and the thermal evolution of lower crustal terranes is strongly related to the production and upward migration of anatectic melts. In turn, the amount of melt that is produced through space and time is controlled by the protolith fertility and the P-T conditions attained during metamorphism.

The lower continental crust exposed in the Ivrea Zone is currently being investigated by DIVE, a scientific drilling project founded by ICDP. In this framework, this study focuses on the chronology and conditions of melting at the crustal depth of site DT-1b, the first borehole drilled in Val d’Ossola. The rock investigated are primarily migmatitic metasediments and amphibolites, which are the two main lithologies occurring in the drilled cores and the surrounding outcrops.

Thermodynamic modelling of selected samples constrains the P-T conditions attained during peak metamorphism to upper-amphibolite facies around 750 °C and 0.7 GPa. Additionally, we estimated melt productivity and the responsible melting reactions for both rock types. Zircon U-Pb dating of residual samples and of the corresponding leucosomes was used to constrain the timing of melting. In particular, metamorphic zircon domains in the leucosome from the amphibolite yield a single age at ~260 Ma. The latter might be related to melt crystallization and cooling following a thermal maximum, which occurred ~25 Ma after the emplacement of the Mafic Complex. Titanite has also been dated to ~265 Ma, in agreement with zircon, suggesting that melting and metamorphic recrystallization occurred within a few Ma.

Instead, zircons from a leucosome in the metasediments record a significantly larger spread of dates from ~300 Ma to ~260 Ma, without a clear statistical peak. This finding suggests that the metasediments at this crustal depth experienced a protracted melting history, occurring over a time interval of ~30 Ma and possibly starting prior the main regional magmatic event.
The structural and lithological control on mineralization at the Upper Cretaceous Sakdrisi epithermal deposit, Bolnisi district, Lesser Caucasus, Georgia

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The Bolnisi district is a part of the Lesser Caucasus and is located at its northern extremity. To the west, this ore district continues into the Eastern Pontides, Turkey. This favorable geotectonic location of the Late Cretaceous Bolnisi ore district (which is also part of the Arvin-Bolnisi Belt) between the Lesser Caucasus and the Eastern Pontides is reflected by its geological diversity, volcanism type and mineral deposit distribution. The Late Cretaceous (~87–71 Ma) bimodal volcanism in this region resulted in mafic and felsic rock types, the latter being a major host of the ore deposits and prospects, and being defined locally as the felsic Mashavera and Gasandami suites. The host rocks of the Bolnisi mining district are represented by Late Cretaceous volcanic and volcano-sedimentary rocks.

Our interpretations and mapping program were undertaken on Sakdrisi 4 and 5. Two complexes have been recognized in this deposit, and belong to the Mashavera suite. They include a lower mineralized volcano-sedimentary complex (LVSC) and an upper barren volcano-sedimentary (UVSC) (Fig.1) complex, which are separated by a NE oriented thrust. The lower mineralized complex is composed of the following lithological units: bedded sedimentary mudstone with tuff interlayers, pumice-bearing volcaniclastic rocks, slightly mineralized rhyolite and rhyolite tuff, and crosscutting explosive breccia, which is well expressed in the Sakdrisi 5 open pit (Fig.2). The upper non-mineralized complex consists of welded and non-welded ignimbrite, limestone lenses and crosscutting andesite-basaltic and rhyodacitic dykes. The mineralized zones are present in the LVSC at certain horizons, and consist mainly in quartz-sulfide and quartz veins, as it was discovered as a bonanza zone located just beneath the thrust zone at the Sakdrisi 4 open pit. Explosive breccia in the system creates a fracture system sometimes together with the regional faults where gold/copper gold bearing quartz and quartz-sulphide veins and stockworks are developing. Recent data from 400–600 m deep drill cores indicate enriched mineralized zones, which is a new discovery for this deposit.
Fig. 2 Lithological units from Sakdrisi deposit: lower banded volcano-sedimentary complex, pumice-bearing volcanoclastic, explosive breccia, welded ignimbrite, gossan like mega breccia, rhyolite flow.

On the Fig 1 is interpreted the 3D model of the Sakdrisi deposit with principal lithological units and main fault zones on Sakdrisi 4 and 5 deposits. The main fault is the central fault which is a thrust fault and also this zone separates the upper non-mineralized units from lower mineralized units. South fault is well outcropping in the Sakdrisi 5 and separates the greenish bedded volcano-sedimentary gypsum bearing horizon from strongly oxidized volcanoclastic pumice-bearing and fine-grained tuff horizons.

In conclusion, on Sakdrisi deposit there is both a structural and a lithological control on mineralization: the fault system created the fractures along which mineralized quartz, quartz-barite and quartz-sulfide and sulfide veins have been emplaced. The explosive breccia is mostly mineralized, even non-mineralized explosive breccia pipe in the close system created very fractured/permeable zones for fluid migration. Clastic/pumice-bearing rocks from Sakdrisi deposit is a good permeable rock, which here is strongly oxidized and mostly gold-bearing.
Evidence for a pre-Himalayan metamorphism in the High Himalayan Crystalline of the Miyar Valley (NW India).

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Most of the tectonic, metamorphic and geochronological data suggest that the Himalaya is essentially the consequence of a single orogenic cycle associated with the India-Asia collision during the Cenozoic era. Therefore, metamorphic assemblages and tectonic structures across the Himalayan range are systematically considered as post-collisional geological records. However, over the last decades, several observations arguing for geological events predating the continental collision have become increasingly recurrent in the literature. Nevertheless, although some of these arguments are thoroughly documented, they are unduly ignored in the construction of models drawing the tectono-metamorphic evolution of the Himalayan range. Yet, the occurrence of a pre-Himalayan history would have considerable consequences on the classical models for the building of the Himalaya.

The recent discovery of inclusions of staurolite crystals in greenschist facies garnets from the Miyar Valley in Upper Lahul region (Himachal Pradesh; NW India) revives the debate on the existence of a pre-Himalayan metamorphism. Indeed, the occurrence of high-temperature staurolites included in greenschist facies garnets suggests that the High Himalayan Crystalline rocks experienced an amphibolite facies metamorphism prior the predominant Himalayan greenschist facies metamorphism observed in this part of the range.

In this study, phase petrology, microtectonic investigations combined with preexisting geochronological data infer that the crystallization of the included staurolite predates the growth of Himalayan garnets. These original data bring new arguments to bear on the long lasting debate of the existence of a Pre-Himalayan orogenic cycle. They lead to the conclusion that the growth of staurolite predates the continental collision between India and Asia and reflects a metamorphic event that belongs to a pre-Himalaya orogenic cycle.
P 2.12
Bulk rock composition and variability of continental lower crust (DIVE project DT-1b, Ornavasso, Val d’Ossola, Italy)

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The Ivrea-Verbano zone, located in the Southern Alps, stands as one of the best studied archetypes of a continental crust-upper mantle section on Earth. Yet, mechanisms controlling the formation of the lower continental crust (LCC) remain enigmatic and highly debated. In the frame of the ICDP funded project DIVE (Drilling the Ivrea-Verbano Zone), questions regarding the formation, evolution and differentiation controlling the bulk chemical composition trough space and time are addressed. Knowledge of the bulk composition of the crust is one target for assembling data and testing key hypotheses.

Preliminary results from the Val d’Ossola DT-1b drill cores are presented with the goal to shed light on the compositional variability of lower crustal metasedimentary rocks. The nearly vertical drilling exposes intercalations of mafic and metasedimentary rocks. Both targeted and random sampling strategies along the 578.8-meter drill core were employed in order to minimize sampling bias. This should provide a ground truth for extrapolating the results towards more realistic assessments of the composition of the LCC. The collected dataset comprises 34 samples representative of felsic metasediments and 15 metamafic samples. Petrographic analyses disclose the predominant composition of felsic metasediments, characterized by biotite schists (Qtz + Pl + Bt ± Grt ± Sil ± Kfs), 28 samples, calc-silicates (Qtz + Pl + Grt + Px + Ttn ± Amp), 1 sample, and para-gneisses (Qtz + Pl ± Bt ± Kfs), 5 samples, while metamafic rocks encompass primarily amphibolites (Amp + Pl +Qtz ± Px ± Bt ± Grt). Note that protholiths of metamafics are not well defined yet and could be from both sedimentary and igneous origin.

Metasediments present a wide range of chemical variability (32 to 89 wt.% SiO₂; 5 to 19 wt.% Al₂O₃; 0.5 to 22 wt.% CaO; 1 to 14 wt.% FeOtot; 0.35 to 0.54 Mg#), likely representative of different protoliths. Metamafic rocks cover a more restricted compositional range (43 to 57 wt.% SiO₂; 11 to 18 wt.% Al₂O₃; 5 to 17 wt.% CaO; 7 to 15 wt.% FeOtot; 0.36 to 0.61 Mg#). Additional data, such as trace element, stable and radiogenic isotopes will further constrain LCC variability. DT-1b data are also compared to regional and global variations in continental and arc lower crust.
Is Apatite a Reliable Mineral for U-Pb TIMS Dating in the Context of Complex Magmatic Regions in the Absence of Zircon?

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The Bolnisi district in Georgia is a distinctive tectonic zone within the Lesser Caucasus, and it is a remarkable segment of the Tethyan orogenic belt with diverse magmatic rocks. Late Cretaceous bi-modal magmatism comprises low-K calc-alkaline to high-K rhyolitic rocks of the Mashavera and Gasandami Suites. They have yielded U-Pb LA-ICP-MS and TIMS zircon ages between 87.14±0.16 Ma and 81.64±0.94 Ma (Hässig et al., 2020; Moritz et al., 2020). High-K calc-alkaline to shoshonitic volcanic rocks of the Campanian Shorsholeti Suite, which represent a later magmatic event, and which stratigraphically overlie the Mashavera and Gasandami Suites. However, the precise age of Shorsholeti, consisting of shoshonitic porphyritic trachyte and trachyandesite remains uncertain due to the absence of dateable zircon. Subsidiary early Eocene adakite-like magmatism magmatism has also affected the Bolnisi district.

In this study, we investigate the U-Pb isotope composition of single crystals of apatite by ID-TIMS and in-situ analyses of major and trace elements by electron probe microanalyzer (EPMA). We want to understand if U-Pb ages of the investigated apatites are consistent with an age range of ca. 87.14±0.16 Ma to 81.64±0.94 Ma obtained on zircons in previous studies. This would mean that apatites could be considered as a geochronometer. Therefore, our primary objective is to determine whether apatite could serve as a reliable mineral for accurate dating in complex magmatic settings in the absence of zircon.

Samples were collected from four distinct areas in the Bolnisi district. Apatites from a trachyandesite sample (BR-1) display a dark blue color under optical cathodoluminescence, elevated La and Ce concentrations, and the highest Sr concentrations (EPMA) compared to the other apatites investigated in this study. Notably, the apatite grains from this site yielded the highest radiogenic Pb over common Pb ratio (Pb*/Pbc), yielding an U-Pb age of 80.04±2.0 Ma. Apatite grains from various rhyodacitic rocks (samples BEQ-2, LG-31, and LG-57) display a range of pale blue to dark yellow colors under optical cathodoluminescence. Apatites from these samples consistently exhibit lower Sr concentrations and a positive correlation between Ce and SiO₂ concentrations is a distinguishing feature compared to the apatites from the trachyandesite. These apatites yielded lower Pb*/Pbc ratios and the calculated dates are significantly younger than 80 Ma and imprecise. For apatites from samples LG-31 and LG-57, local overprints from Eocene magmatism are suggested. These apatites have higher La and Ce concentrations compared to sample BEQ-2, suggesting distinct local influences of post-mineralisation fluid alteration.

Our findings demonstrate that apatites from shoshonitic trachyandesite yield a reliable age with a moderate uncertainty of ~2.5%, indicating that they can be used as an alternative for dating magmatic rocks lacking zircons. The BR-1 date also coincides with the age of shoshonitic rocks in the Eastern Pontides, NE Turkey, which is considered as the western extension of the Bolnisi district (Moritz et al., 2020). Nonetheless, it is recommended to evaluate the data with caution, since apatite U-Pb isotopes could be disturbed or behaves as (partially) open systems during overprinting magmatic activity or the waning stages of fluid circulation. Depletion in Ce, La, and Sr indicates possible metamorphic or fluid alteration of the BEQ-2 samples, while higher Ce and La concentrations vs. Sr depletion might imply the influence of later stage Eocene magmatism for LG-31 and LG57 samples, that may have generated a compositionally different fluid percolating within the rocks studied in the Bolnisi district.

In conclusion, our study reveals significant differences in cathodoluminescence color and geochemical patterns between magmatic and hydrothermally altered apatites. This research substantially contributes to our understanding of utilizing apatites for U-Pb ID-TIMS dating in magmatic rocks lacking zircons. Furthermore, it enables dating a shoshonitic magmatic pulse within the Bolnisi District, Georgia, and is contributing to a better understanding of magmatic processes, tectonic dynamics, and constraining the geodynamic framework of the central Tethyan orogenic belt.
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Figure 1. Apatite grains A) magmatic apatites from the shoshonitic trachy andesite of the Shorshorleti suite; B) altered apatites from rhyodacite of the Gasandami suite.
**P 2.14**

**Tectono-magmatic origin of aligned intrusions in the Damaraland igneous province, Namibia: new evidence from high-precision zircon dating and geochemistry**

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Early Cretaceous intrusions in the Damaraland igneous province (Namibia) display a SW-NE alignment. They are related to the Paraná-Etendeka Large Igneous Province (LIP), but their magmatic origin and timing of emplacement within the LIP evolution are still enigmatic. We use zircon geochronology, Hf isotope compositions, and bulk rock/zircon geochemistry of these intrusions to decipher the spatial pattern of magmatism and the mechanism(s) of magma formation and evolution. High-precision CA-ID-TIMS zircon ages show that the plutons were emplaced without clear spatial systematics over at least 1.4 My (133.2-131.8 Ma), around/after the 135-133 Ma volcanic activity peak in the southern Etendeka (Namibia) and the Paraná (Brazil). The youngest Damaraland zircon ages overlap with previously reported baddeleyite ages for highly evolved sills in the Southern Paraná, confirming that magmatism in the LIP continued beyond 132 Ma. In the whole Damaraland province, intrusive rocks follow two distinct evolution paths towards both the granite and the phonolite minima. Absence of spatial trends along the aligned complexes in both geochemistry and crystallization ages argues against plate movement over the Tristan-Gough plume as the origin of these complexes. Instead, lithospheric extension along reactivated lineaments led to near-synchronous melt generation across the province. Negative zircon εHf(t) values in silicic complexes (-5 to -12) likely arose from path contamination of melts from a +/- metasomatized mantle source(s) during ascent, while in average less negative εHf(t) in alkaline/carbonatitic intrusions (-2 to -6) reflect source contamination and stem from the preferential melting of mantle portions metasomatized by the Tristan-Gough plume.
P 2.15
Garnet multi-component diffusion modelling reveals local heat sources affecting the cooling history of the Lepontine dome

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The Lepontine dome (Central European Alps) is a metamorphic and structural dome formed by crystalline basement nappes accreted during the Alpine continental collision in the Eocene-Oligocene. The dome is characterized by a widespread Barrovian metamorphism. The peak amphibolite-facies conditions coincide with the final phase of nappe emplacement at ca. 31 Ma, dated via U-Pb zircon dating of syn-tectonic migmatites along the principal shear zone at the base of the Maggia-Adula nappe.

The duration of the cooling following the temperature peak is still not well contrained. Therefore, in this contribution we evaluate the apparent cooling rates of paragneisses within the Lepontine dome through inverse diffusion modelling in garnet. Our working procedure consists of: (i) analysis of garnet-rims compositional re-adjustment and (ii) comparison of the obtained cooling rates with 1-dimensional thermal models. We examined six garnet-paragneisses collected at different structural levels within the Lepontine nappe stack. The selected garnet crystals show at their rim a coupled Mg-decrease and Mn-increase, indicative of post-peak temperature retrograde modification. We applied geothermobarometry to determine the post-peak re-equilibration conditions and we obtained a cooling rate distribution which varies spatially within the study area. The highest cooling rates are within the Maggia-Adula shear zone, whereas at the base of the footwall nappe the cooling rates are very low. In the migmatitic Southern Steep Belt which borders the Lepontine dome to the south, apparent cooling rates have intermediate values.

These results compared with thermal models permit to identify regional patterns related to geodynamic processes. The high cooling rates obtained within the main thrust cannot be explained by regional exhumation processes, but a transient local heat source has to be invoked. An additional spatially-confined heat source can be represented by hot fluids percolation or shear heating.
P 2.16
Petrologic and sedimentological investigations on boulders of the river Dreisam (Black Forest, FRG)

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In a larger study, the rivers of the Black Forest, their debris and their impact on the sediments of the Rhine River were investigated. In the framework of this project, petrologic and sedimentological studies on boulders carried by the river Dreisam and its headstreams were performed. For this purpose six different locations were sampled, from the headwaters in the Zartenbach to the western limits of the city of Freiburg im Breisgau (Baden-Württemberg, Germany).

The 29.7 km long river Dreisam flows along the border of the Central and Southern Black Forest. The bedrock in the Black Forest was originally deposited in the Precambrian or Early Paleozoic and underwent various metamorphic imprints as well as magmatic processes (Metz & Rein 1958). The main metamorphism took place 330–335 Ma ago during the Variscan orogeny (Kalt et al. 1994). Thus, mainly metamorphic and magmatic boulders were expected. The samples were investigated by thin sections and Raman spectroscopy to analyze the mineral composition and to decipher their origin. Sedimentologically, the roundness and sphericity of the boulders were determined as well as the evolution of these measures along the course of the river and related geomorphological features.

At the first sampling point in the headstream Zartenbach, almost exclusively paragneisses were detected. Due to the strong weathering and strain, a macroscopic identification of the boulders was often challenging. Thin sections revealed a distinct compositional banding with mafic hornblende- and biotite-rich layers as well as felsic sections with minor to intermediate anatectic features. According to the geological map (Groschopf et al. 1996) the paragneisses constitute a large complex in the source region of the river.

At the second sampling site (Ravennaschlucht), the large majority of boulders could also be assigned to the paragneisses. However, a certain amount of distinctly migmatic meta- and diatexites occurred showing fluent petrographic transitions. These rocks often contained prominent amounts of cordierite and sometimes garnet.

At the third sampling site (Höllental), boulders of meta- and diatexites with a marked increase in the degree of melting dominated. One sample with a very high degree of melting even showed nebulitic features.

At the fourth sampling site, where Höllen- and Wagensteigbach unite to the river Dreisam, felsic igneous rocks appeared for the first time forming well-rounded and spherical blocks. Very quartz-rich, fine-grained aplites, microgranites and a rhyolite were found. These magmatites very probably originated from small dikes in the vicinity of the Höllenbach (Groschopf et al. 1996). Besides minor paragneisses and diatexites, an augengneiss was also detected.

At the fifth sampling point in the eastern suburbs of Freiburg, in addition to the various crystalline rocks (para- and orthogneisses, rhyolites and aplites), fine-grained amphibole gneisses to amphibolites occured. Thin sections gave proof that three of the mafic rocks were retrograde eclogites displaying symplectic intergrowths of albite and diopside replacing primary omphacite. Furthermore, relic garnets were mantled by coronitic aggregations of tschermakite and plagioclase.

The sixth sampling point in the western outskirts of Freiburg mainly supplied paragneisses and migmatites as well as a few granitic rocks. There, the only small pebble of clay-rich sandstone occurred, which likely originated from the nearby outcrops of Mesozoic sediments (Groschopf et al. 1996).

Our investigations highlight the dominance of metamorphic rocks in the spectrum of boulders in the river Dreisam, which is due to the massive complexes of paragneisses and migmatites in the central Black Forest area. Magmatic rocks mainly originate from subsequent felsic dykes whereas sedimentary rocks almost lack completely. The crystalline rocks are often affected by a late, low-grade hydrothermal alteration leading to the formation of prehnite, chlorite and carbonate.

Downstream, a general trend of increasing sphericity (S) and roundness (R) is evident for the studied boulders and pebbles, from S = 0.37 and R = 0.33 in the source area to S = 0.40 and R = 0.66 close to the confluence with the Rhine River. The graph (Fig. 1) nearly follows the ‘growth’ curve reported in literature (e.g., Pettijohn, 1975). Isotropic granite pebbles slightly differ from anisotropic gneisses in these textural measures. Deviations from the trend appear to be related to erosion of glacial terraces.
Figure 1. Trend line of the sphericity of gneisses and granites along the river.

REFERENCES
Recovery of the first camera-observed meteorite fall in Oman

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In recent years, meteor cameras which scan the night sky for fireball events have yielded numerous observations all over the world. As the landing site of a meteorite can be modelled based on the fireball trajectory, a number of freshly fallen meteorites were retrieved thanks to those camera systems. Freshly fallen meteorites with camera observations are of particular importance to meteorite science. For instance, the orbit of the meteoroid around the sun can be calculated from the camera data. This helps to establish a link between a specific meteorite material and a location in the solar system.

Four sky observation cameras were installed in the desert of Oman in 2022 as a part of a collaboration between Swiss and Australian researchers and the Ministry of Heritage and Tourism in Oman. During the first year of observation, 19 fireballs were observed by the cameras in Oman. Of those, 13 were observed by two or more cameras, effectively enabling the triangulation of the falling meteorite. In a field campaign in February 2023, two promising target areas were searched. This led to the recovery of two fresh-looking meteorite pieces near Al-Khadhaf. The temporal link between camera observations and the recovered meteorites was established by gamma spectrometry. The presence of the short-lived cosmogenic nuclides 54Mn (t1/2 = 312 d) and 22Na (t1/2 = 2.6 a) confirmed the young (~1 a at the time of find) terrestrial age of the meteorite. The meteorite is an ordinary chondrite containing clasts of differing metamorphic degree, classified as a H5-6 breccia. The calculated trajectory indicates that the meteorite derived from the inner part of the asteroid belt. At the time of submission of this abstract, the meteorite is awaiting official recognition by the meteorite nomenclature committee. At the conference, we will present the recovery of the meteorite and discuss the results of the petrography, gamma spectrometry as well as the orbit and possible origin of the meteorite in the solar system.

REFERENCES
The overlooked role of tropical trees in supporting biotic and abiotic Ca carbonate precipitation

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The formation of pedogenic carbonates (PC) occurs via abiotic and biotic processes leading to the formation of minerals with various morphologies and isotopic composition ($\delta^{13}C$), depending on the local environmental factors (Zamanian et al 2016). The oxalate-carbonate pathway (OCP) is a peculiar biogeochemical succession of reactions leading to the accumulation of PC species in tropical acidic soils, where there is no geogenic carbonate rocks. The OCP develops in specific plant-soil systems where biological activity promotes the accumulation of Ca$_2^+$ ions, e.g., in plant cells and the rhizosphere, and where the oxalate species i) is formed as by-product of photosynthesis, ii) accumulates in different plant parts, and iii) is subsequently oxidized by oxalotrophic bacteria and fungi associated to plant wounds or during leaf litter degradation. The accumulation of bicarbonate ions in the local environment, as a byproduct of the bacterial metabolism, induces an increase in alkalinity, and consequently of pH values, promoting mineral precipitation when supersaturation conditions with respect to CaCO$_3$ are reached (Pons et al. 2018).

The iroko tree (Milicia excelsa) in Ivory Coast has been reported to present calcite-cemented sandstones associated to wounds on trunks and in the rhizosphere where the soil pH can locally rise to 8, while the surrounding ferralic soil displays pH between 4 and 6 (Pons et al 2018). The presence of Ca-carbonate in this ecosystem has attracted increasing attention as a potential underestimated sink for inorganic C (up to 6 kg of C/year in soil) (Cailleau et al 2011). However, the complex array of abiotic and biotic reactions underpinning the carbonate precipitation process leading to various types of mineral facies are not yet well understood.

In this study, we propose a systematic investigation of few soil-iroko systems in Ivory Coast, with the aim of elucidating the link between different types of CaCO$_3$ facies associated to the trees and their specific precipitation processes. To this purpose, soil samples were collected to quantify pH, oxalate and carbonate contents, as well as the cation exchange capacity at different depth and distances from the studied plants. Macro-samples (from 1 cm to 50 cm long) of plant materials and petrified wood were collected in the aerial parts of the plant and in the rhizosphere (e.g., trunk and roots). Standard petrographic analyses (associated to cathodoluminescence, UV light and Scanning Electron Microscopy) were used to observe the different types of CaCO$_3$ facies. Powders of such macro-samples were collected using a microdrill to determine the $\delta^{13}C$ values of the organic material and the carbonate phases to calculate $\Delta^{13}C$carbonate-org values. Obtained results show unequivocally that the carbon in the carbonate phases mainly derives from organic molecules synthesized through the photosynthesis, i.e., from atmospheric CO$_2$, and that carbonates are mainly associated to the rhizosphere or directly replace plant material. However, several different forms of carbonate are present in a same soil-plant system (i.e., micrites and sparites). Isotopic and petrographic investigations suggest that CaCO$_3$ precipitation occurs concomitantly through abiotic and biotic processes (e.g., climatic effects and biomineralization induced by natural CO$_2$ degassing). Additionally, the large window of $\Delta^{13}C$carbonate-org values indicates the occurrence of carbonate precipitations outside the range of equilibrium conditions (Prud’Homme et al 2018) suggesting the presence of consecutive dissolution/reprecipitation phenomena (early diagenesis) due to microclimate effects, as well as a mix of organic molecule precursors leading to a range of carbon sources in carbonates (e.g., oxalate, latex, acetate associated to termite activity). Overall, this work shows that the iroko tree is an overlooked reactor permitting the CO$_2$ transformation, first in biomass, and later, in an alkalinity/CaCO$_3$ engine.

REFERENCES

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