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2.1
A new map of the Oman ophiolite extrusives: insights into protoarc crust composition, boninite distribution and sulphide deposit prospectivity


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Studies of Western Pacific arc basement indicates that vast swathes of ‘protoarc’ oceanic crust 100s of km wide and 1000s of km long form during subduction initiation events prior to the establishment of steady intra-oceanic subduction. A similar tectonic setting for the formation of the Tethyan ophiolite chain has been inferred from their remarkable structural, geochemical and geochronological similarities with the West Pacific protoarc record.

The petrogenesis of the characteristic volcanic rock types of these settings—forearc basalts and boninites—are reasonably well understood, however, very little is known about their abundance and distribution in poorly preserved protoarc crust. With this in mind, the Semail ophiolite (Oman–U.A.E.)—the world’s largest and most complete subaerial exposure of oceanic crust—provides a prime opportunity for a quantitative consideration of the different volcanic rock types in protoarc crust. Uplift and erosion of the ophiolite has exposed a 300 km long strip, or ~500 km2, of volcanics in a gently east-dipping cross section along the northeastern margin of the Hajar mountains. This simple structure, the lack of vegetation, and the abundance of previous petrogenetic studies on the extrusive sequence means that the spatial distribution of each volcanic episode is well-testable in map-view.

We have collated geochemical analyses and maps from the literature and collected and analysed a further 200 samples from the ophiolite to better define the field, geochemical and magnetic characteristics of its volcanic units. These characteristics were then used during field and aeromagnetic mapping of the lava units both in outcrop and under sedimentary cover throughout the northern ophiolite. The resulting map provides a new framework for research in the ophiolite extrusives, it sets the first constraints on the relative abundance of boninites in Oman, and it provides a new tool for targeting Au-enriched volcanogenic massive sulphide deposits hosted in these boninites.

2.2
Sulphuric acid-mediated weathering on Taiwan buffers geological sinks of atmospheric carbon

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The chemical composition of the Gaoping River in Taiwan reflects the weathering of both silicate and carbonate rocks found in its metasedimentary catchment. Major dissolved ion chemistry and radiocarbon signatures of dissolved inorganic carbon (DIC) reveal the importance of pyrite-derived sulphuric acid weathering on silicates and carbonates. Two-thirds of the dissolved load of the Gaoping River derives from sulphuric acid-mediated weathering of rocks within its catchment. This is reflected by low DI14C signatures, with rock-derived carbonate constituting a 14C-free DIC source. Using an inverse modelling approach, we provide quantitative constraints of mineral weathering pathways and calculate atmospheric CO2 fluxes resulting from the erosion of the Taiwan orogeny over geological timescales.
2.3
What can we learn from $\delta^{18}$O in olivine-hosted melt inclusions?

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Melt inclusions are small droplets of melt trapped during crystal growth. They are often used to trace primary magmatic processes possibly lost in whole rocks, especially when trapped in olivine (e.g., Kent, 2008). The majority of the data from olivine-hosted melt inclusions (OHMIs) consists of major, volatile and trace elements. OHMIs usually show large chemical variability, which can result in term of post-entrapment processes (element diffusion, host crystal crystallization, bubble growth), crystallization process (e.g., boundary layer) or source process (e.g., fluid contributions, melting rates...). A few studies reports stable isotopes in OHMIs (e.g., Hauri et al., 2002; Rose et al., 2001). The large range of compositions measured for different stable isotopes were interpreted in term of fluid input(s) into the mantle wedge (arc settings) or magma mixing and crustal assimilation (Iceland) (e.g., Bouvier et al., 2008; Hartley et al., 2013).

A recent study of $\delta^{18}$O in OHMIs from 2 MORBs samples show an individual range of isotopic variations up to 2.5‰ (Manzini et al., submitted), whereas the average bulk rock $\delta^{18}$O for fresh unaltered MORB is 5.5 ± 0.3‰. Oxygen isotopes variation in OHMIs from the 2 different samples is not correlated with any trace element ratios nor volatiles, suggesting that the variability is not linked to a source process. For each sample, only ~40% of OHMIs are in isotopic equilibrium with their host. This population of OHMIs show rather small variation, suggesting limited (<1‰) source heterogeneity. The current dataset suggest that the measured variability is mostly due to true syn-entrapment O diffusion, but the exact physical process responsible for the disequilibrium remains unclear.

For arc samples, larger $\delta^{18}$O variations are expected, because fluids are involved in the magma genesis of most arc magmas. For example, OHMIs in samples from 5 different arcs only show a maximum of 2.7‰ variation within a sample (Bouvier et al., submitted), similar to the isotopic range measured in the MORB samples. Also, in one arc sample for which $\delta^{18}$O was measured in the host olivine, ~40% of OHMIs seems to be in isotopic equilibrium with their host, a proportion similar to that found in the MORB samples. This suggests that the process generating olivine-MI isotopic disequilibrium (lower and higher partitioning values) is not MORB specific. A better understanding of the processes generating the oxygen isotopic disequilibrium between MI and their host olivine from various samples may bring new information about MI entrapment processes, crystal growth and/or magma transport.

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2.4
Garnet as a key mineral to trace the origin of fluid-rock interactions in high grade metamorphic rocks (Western Alps, Switzerland)

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Fluids are known to play key roles in subduction interface processes. Water-rock interaction at the ocean floor hydrates the mafic crusts and the underlying mantle. During subduction, mineral dehydration reactions in the different rock types constituting the slab produce fluids that interact with nearby rocks and can lead to the formation of metasomatic reaction zones. The Theodul Gletscher tectonic Unit outcrops within the Zermatt Saas ophiolite (Western Alps) consists of an association of micaschists and mafic boudins resting on serpentinites that underwent eclogitic facies metamorphism during Alpine subduction (2.4±0.1 GPa and 550±50 °C). Schists located close to a mafic boudins systematically display textural evidences for fluid-rock interaction suggesting heterogeneous fluid activity and permeability at the outcrop scale.

The bulk rock chemistry of the mafic rocks displays high CaO concentration ranging from 15.9 to 22.4 wt% and low Na2O and MgO concentration ranging from 0.3 to 0.5 wt% and from 4.3 to 11.3 wt% respectively. These major chemical variations are typical for alteration process occurring at the seafloor by interaction with seawater prior to subduction. Rare earth element (REE) patterns show strong enrichment in light-REE.

Garnet was targeted in order to characterise the fluid rock interaction along the P-T evolution. This metamorphic mineral is present in every lithology of the tectonic unit and can preserve prograde to peak metamorphic zoning for major elements. After investigation under BSE imaging and EPMA mapping garnets show evidence of a multi-stage evolution. At the contact zones between the schists and the high-grade boudins, euhedral garnet porphyroblasts are observed within the schists. The size (ranging from tens of µm to several cm in diameter) and abundance of garnet increase towards the contact. In the schists, the largest garnet grains are composed of a Fe-Ca-rich core (of possible pre-Alpine origin), a Fe-Mg-rich mantle and a Ca-rich rim. The textural relationships between the garnet compositions suggest a replacement of the core by the second generation and fracture filling occurring together with rim-core replacement during rim growth of the last generation. Garnets in the mafic rocks show both normal growth zoning and replacement textures with an increase in grossular content from core to rim.

In situ oxygen isotope analyses of garnet porphyroblasts from the schists show a marked change in δ18O signatures from 12‰ in the core to 4‰ in the rim. This decrease is coherent with chemical zoning observed for major elements. Garnet from the mafic boudins has δ18O values from 0.5 to 2‰. The strong variations in oxygen isotopic composition are evidence for open system behaviour. This petrological, micro-textural and geochemical investigation highlights multiple stages of fluid exchanges and possibly diverse fluid sources and pathways from seafloor alteration to peak metamorphism.
2.5 Oxygen isotopes in white mica from the Larderello geothermal field – a tool to trace fluid flow in a complex magmatic – hydrothermal system

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White mica is present in all major stratigraphic units in the Larderello geo-thermal field (LGF) including the metasedimentary units that form the “upper reservoir” (UR) as well as the granite intrusions and the contact metamorphic basement that constitutes the actively exploited “lower reservoir” (LR). Texturally and chemically distinct generations of white mica record stages of magmatic crystallization, thermometamorphic/hydrothermal replacement and fluid/rock interaction in the dynamic environment of the LGF. The chemical and \(^{18}\)O/\(^{16}\)O composition of white mica varies at the intra- and inter-grain scale. The majority of the analysed white mica can be classified as muscovite (K: 0.93±.03, 1σ, Si: 3.1±.1, \(^{20}\)Al: 1.8±.1; apfu, per 11 oxygens). The compositional variability is the result of three dominant cation exchanges, 1) paragonite-muscovite [K—Na], 2) Tschermak [Si+(Mg, Fe)—2Al] and 3) pyrophyllite [(K, Na)—]. The shift in \(^{18}\)O reflects varying degrees of fluid/mineral interaction with either dominantly low-\(^{18}\)O (meteoric) or high-\(^{18}\)O (magmatic) fluids. Granite and contact metamorphic lithologies (micaschist and gneiss of the crystalline basement) contain white mica with overlapping crystal chemistry (mostly due to exchange 1 and 2), whereas the metasedimentary white mica show the highest variation via exchange 1 and 3. In-situ Secondary Ion Mass Spectrometry (SIMS) \(^{18}\)O/\(^{16}\)O analysis of white mica resolve the fluid/mineral interaction on microscale and identifies a dramatic spread of \(^{18}\)O values between ~1–14‰. Metasediments (phyllite and quartzite) from the UR inherit this large spread in \(^{18}\)O, with texturally and chemically distinct white mica populations (Fig.1) ranging from late hydrothermal (~1–6‰; low Na, mid Mg apfu), over partially altered (\(^{18}\)O=8–9‰; low Na, low to mid Mg) to detrital (\(^{18}\)O=14‰; high Na, low Mg). The \(^{18}\)O values of the detrital white mica resembles that of bulk unaltered micaschist from the Northern Appenines (Gianelli and Ruggieri, 2002), whereas the late hydrothermal white mica has similar \(^{18}\)O values to other secondary minerals and the meteoric-dominated fluid circulating in the late hydrothermal stage (present day temperatures up to 450°C; Petrucci et al., 1994). Downhole towards the LR, white mica from two contact metamorphic micaschist samples shows either 1) homogeneous \(^{18}\)O values of ~9‰ that were likely re-homogenized during the early hydrothermal stage, or 2) large spread in \(^{18}\)O from 2 to 12‰ in grains of variable texture and chemistry. The later micaschist sample is cross-cut by a thin high-temperature hydrothermal vein with texturally different white mica than the host rock, but both populations display the same spread in \(^{18}\)O values. Two granite samples from Carboli contain chemically variable white mica with a homogeneous primary magmatic \(^{18}\)O of ~10‰, whereas two older granite samples from Radicondoli have instead heterogeneous magmatic to hydrothermal white mica with variations in \(^{18}\)O of ~4–10‰. The pronounced intra-grain \(^{18}\)O variability of up to 6‰ in this white mica occurs in domains with higher Fe and Mg around chlorite inclusions, as a result of interaction with low-\(^{18}\)O fluids that perculated downwards to depths of 3–5 km through extensional shear zones (Bellani et al., 2004).

The new microscale \(^{18}\)O data of white mica at the LGF reveal that 1) \(^{18}\)O/\(^{16}\)O exchange is not necessarily coupled with major element exchange and white mica recrystallization, 2) \(^{18}\)O/\(^{16}\)O variability occurs and persists at the µm-scale in an active geothermal field and 3) localized infiltration of low-\(^{18}\)O fluids occurs with little fluid/rock interaction along faults, fractures and cleavages down to ~4.6 km.
Figure 1. Back-scattered electron (BSE) images of muscovite populations in quartzite from the UR with corresponding $\delta^{18}$O values versus Mg content.

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2.6 Formation of felsic lower continental crust: insights from U–Pb geochronology of detrital zircon from lower crustal granulites

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The European Alps and the wider European area preserve numerous fragments of Variscan lower continental crust that have been widely studied to document the Permian extension, Jurassic continental rifting and Tertiary Alpine orogeny that reworked and ultimately exhumed these fragments of lower crust. Relatively little attention has been paid to the nature and formation of this lower crustal crust prior to its Carboniferous–Permian evolution. Of particular interest is the widespread occurrence of felsic lithologies in these lower crustal relics, including in the classic example of the Ivrea Zone (Italy). High seismic velocities and the common occurrence of mafic lower crustal xenoliths have lead to the lower continental crust traditionally being interpreted as dominantly mafic in composition (e.g. Rudnick and Gao, 2003). This view has recently been challenged, with the suggestion that a considerable proportion of the lower crust could be felsic and metasedimentary (Hacker et al., 2011). The composition of the lower continental crust has fundamental implications for the thermal, rheological and seismic velocity characteristics of the crust, as well as for models of crustal differentiation and reworking. Constraining the nature and formation of felsic lower crust from the European Alps has the potential to inform this debate.

In this study we use detrital zircon cores preserved in Permian granulite facies metapelites from the Malenco Unit (Eastern Alps, Italy) to characterise felsic lower crust from a crust–mantle transition zone. U–Pb geochronology of zircon cores that show clear textural evidence for a detrital origin gave an age spectrum recording the major orogenies known to have affected Gondwana, in particular the Pan-African (650–500 Ma) and Caledonian (450–400 Ma), with subordinate Precambrian detritus with ages up to ~2.5 Ga. Th/U ratios >0.2 for the detrital cores suggest that detritus was dominantly derived from eroded magmatic sources. The presence of a significant population of 450–400 Ma detrital zircons indicates that deposition of the sedimentary protolith occurred after 400 Ma, and thus after the Caledonian orogeny. Exclusively Permian ages for metamorphic zircon rims in the same samples record granulite facies conditions associated with gabbroic underplating during extension following the Variscan orogeny. Our results demonstrate that uplift and erosion of igneous source rocks, deposition of the sedimentary protolith, and transport of the protolith from the surface to lower crustal conditions all occurred within a single orogenic cycle. The absence of a significant population of either detrital or metamorphic zircon with Carboniferous ages indicates that the Malenco lower crust did not experience significant partial melting during the Variscan orogeny. This contrasts with lower crustal relics from the Bohemian Massif, which document widespread anatexis at (U)HP–UHT conditions during Variscan continental subduction (e.g. Bröcker et al., 2009; Walczak et al. 2017). The new geochronological constraints for the Malenco granulites will be integrated with zircon trace element analysis and Ti-in-zircon thermometry, as well as petrological constraints for the host granulites, to explore implications for the timescales and mechanisms of formation of felsic lower continental crust.

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2.7
Magmatic sulphide saturation in subduction and post-subduction magmas

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Porphyry deposits are associated with both subduction and post-subduction settings. In both geodynamic settings the fertility of the magma is thought to be controlled mainly by an incompatible behaviour of economic chalcophile metals during magmatic evolution as well as their partitioning into an exsolving fluid phase before they become sequestered by magmatic sulphides.

The main aim of this project is to constrain the physicochemical conditions under which magmatic sulphide saturation occurs and investigate its possible role for the processes of ore genesis during magmatic evolution in two different geodynamic settings above by studying magmatic sulphide inclusions (MSI) in volcanic complexes and in their enclaves. The geological areas investigated are: (a) the Quaternary Ecuadorian volcanic arc, hosting, among others, the Llurimagua Cu-Mo and Cascabel Cu-Au Miocene porphyry deposits (subduction setting), (b) the Miocene volcano-plutonic complexes of Konya (hosting the Doganbey Cu-Mo-W porphyry and Inlice Au-epithermal) and Usak (hosting the Kisladag 5.5 Moz Au porphyry), in Western Turkey (post-subduction setting), (c) the Kula Plio-Quaternary volcano, in the Usak basin, in Turkey (intraplate OIB-like signature volcano in post-subduction setting), and (d) the active volcanic center of Nisyros in Eastern Greece with no direct porphyry deposit association (subduction setting).

In most investigated areas (except the Kula volcano most mafic rocks with OIB signatures) Cu behaves as a compatible element, showing a decreasing trend with magmatic evolution, indicating that Cu is lost/stored on the way to the surface within the continental crust (Chiaradia, 2014).

The following preliminary results on petrography and mineral chemistry include only the areas of Ecuador, Konya and Kula (data from Usak and Nisyros are in the process of acquisition).

From petrographical observations MSI were found in different amounts in all investigated rocks covering a wide compositional range (SiO2=47-67 wt.% and MgO=6.5-1 wt.%), indicating that in both subduction and post-subduction settings, sulphide saturation occurs throughout magmatic evolution. In all study areas MSI display similar texture and host mineral (mostly globular, up to 40 μm in size and hosted by magnetite crystals, see Georgatou et al., 2018 for details) with the exception of Kula volcano. Kula presents larger MSI (up to 200 μm) hosted mainly by pyroxene (and amphibole) and found also in the groundmass as oxide-sulphide aggregates.

From microprobe analyses MSI from Kula (whole rock Cu mean=29 ppm) are unusually Cu-poor and Ni-rich with maximum contents of 32.5 and 25.9 wt%, respectively, compared to those of Konya (whole rock Cu mean=12.5 ppm) and Ecuador (whole rock Cu mean=27.5 ppm), which are mostly hosted by magnetite and have maximum Cu and Ni contents of 73 and 9 wt%, and 65.7 and 10 wt%, respectively. This implies that Cu is getting more efficiently sequestrated in Konya compared to other investigated magmatic provinces.

A general observation resulting from petrography and mineral chemistry is that the Cu-poorest MSI are hosted by olivine (and less by amphibole) phenocrysts and show usually globular shapes whereas the Cu-richest MSI are found in magnetite crystals and are usually smaller and rectangular, indicating that the sulphide phase was entrapped as a melt and crystallized along the crystallographic planes of the mineral (Georgatou et al., 2018). This may indicate a two stage magmatic sulphide saturation process: an early stage crystallizing Cu-poor MSI (composed of both mss/iss) and a later stage producing only Cu-rich MSI (also seen by others, e.g. Agangi & Reddy, 2016).

Preliminary results indicate that enclaves (and especially the ones rich in amphibole and pyroxene) carry in all study areas a greater amount of MSI compared to the host rock. In addition both Ecuador and Konya enclaves carry MSI which are Cu-poorer compared to the ones found in the host rock, whereas Kula MSI found both inside and outside of the enclaves seem to have similar composition.

Further mineral analysis (also by LA-ICP-MS), thermobarometry and Qemscan analysis on enclaves are needed to investigate the timing/P-T conditions of sulphide saturation (early vs late) in the crust.

REFERENCES


2.8 Melt inclusions and crustal anatexis at ultra-high temperature conditions

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Deep levels of the continental crust can attain, on a regional scale, extreme thermal regimes, such as ultra-high temperature (UHT) metamorphism. At these conditions, in which temperature exceed 900 °C, rocks buffer the increased thermal gradient undergoing partial melting, a process that is believed to control the geochemical differentiation, reworking and rheology of the lower crust. The Gruf Complex in the European Central Alps is a 12 x 10 km migmatitic body embedded between the Penninic units of the Alpine nappe stack and some Tertiary intrusions. The main rock types outcropping in the Gruf Complex consist of migmatitic orthogneisses, paragneisses and micaschists, leucogranites and charnockites. Migmatitic orthogneisses and charnockites are characterized by the presence of UHT granulites, which occur as schlieren and massive enclaves and that represent residual rocks after anatectic crustal melting. The granulitic enclaves are mostly composed of prismatic sapphirine, up to 2 cm large garnet porphyroblasts, Al-rich orthopyroxene, sillimanite and cordierite. Porphyroblastic garnets contain numerous trapped melt inclusions (MI), which are preserved as both hydrous glass coexisting with CO₂ bubbles and crystallized nanogranitoids. These MI have variable sizes, ranging from 5 to 100 µm in diameter. Larger MI are irregular in shape and display offshoots, while tiny inclusions are more isometric. Commonly, crystallized MI contain biotite and/or muscovite, quartz, feldspars, apatite and minor oxides. Rare polycrystalline inclusions also occur within sapphirine. These inclusions often display a negative crystal shape and typically are less than 20 µm in size. Preliminary experiments with a piston cylinder apparatus show that nanogranitoid inclusions can be rehomogenized at temperature between 850-900 °C and thus allow to constrain the original composition of the melt. Melt inclusions in the Gruf granulites are interpreted to represent early anatectic melts produced during incongruent, fluid-absent melting reactions and have therefore the potential to shed light on the crustal reworking processes associated with UHT metamorphism.
2.9
Metamorphic resetting explains the Hf and Nd paradox in Eoarchean rocks

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Recent models argue for extensive early differentiation of the silicate Earth and formation of voluminous, stabilised continental crust by 3.5 Ga. Consequently, the most ancient samples of continental crust have attracted significant attention, in order to determine the scale and mechanism of early continental growth and mantle-crust differentiation. Eoarchean crustal rocks are therefore key to gain unique insights into the evolution of the Earth’s mantle and crust. Interestingly, some rocks representing this ancient continental crust show complicated, decoupled Nd and Hf isotope signatures. While Hf isotopes point to a chondritic source, Nd isotopes have a superchondritic signature, which is inconsistent with a common origin. Explaining and understanding this inconsistency is critical in order to gain insights into Eoarchean crust-mantle differentiation processes at the beginning of crust stabilization on our planet. However, thus far no general agreement has been reached to explain this conflict of isotope signatures. Moreover, some current models invoke speculative processes to explain the Hf and Nd isotope fractionation, such as the presence of magma oceans and Eoarchean subduction zones.

In this study, we investigate which minerals control the Sm-Nd isotope system in Eoarchean meta-igneous rocks that show apparent Hf and Nd isotope decoupling. Our results demonstrate that isotopic resetting during post-emplacement metamorphic processes play a key role in “decoupling” Hf and Nd isotopes. Metamorphic disturbance of the Sm-Nd isotope system is capable of shifting the Nd isotope signature to both more and less radiogenic values, creating apparent Hf and Nd isotope inconsistencies and challenging other models for explaining the Hf-Nd paradox.
2.10

Fast H loss from hydroxylated Si vacancies in experimentally dehydrated olivine

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Knowing the diffusivity of hydrogen in olivine is crucial not only for geospeedometry (diffusion chronometry) applications, but also for constraining the potential for olivine-hosted water to enter the deep mantle. Experiments in pure forsterite (+Ti⁴⁺) (Padron-Navarta et al., 2014) and observations in the natural assemblage (olivine+antigorite+chlorite+magnetite) from subducted olivine-bearing serpentinites [2] suggest that H associated with the tetrahedral site, i.e. 4xH⁺ charge-compensating a Si⁴⁺ vacancy is extremely retentive in olivine. We extended the study from synthetic forsterite to natural Fe-bearing olivine (Mg#≈0.95=(X₄Mg/(X₄Mg+X₄Fe))), by dehydrating natural olivine-bearing rocks (same assemblage as above) from Zermatt, Switzerland (Kempf and Hermann, 2018) where all H⁺ in olivine is associated with the tetrahedral site. Rock pieces were annealed at 1 bar, oxygen fugacity of ~QFM to QFM-5, 875 °C, for one hour, then samples were doubly polished to 100-150µm, and analysed by Focal Plane Array (64x64 bit detector) Transmission Fourier Transform Infrared Spectroscopy to map the resulting OH distribution. We find that 1) serpentine breakdown occurs in a matter of seconds, forming enstatite, thus considerably modifying the silica activity of the system 2) a series of new OH stretching bands grow during dehydration and 3) H loss is considerably (several orders of magnitude) faster than the previous experimental determination in pure forsterite. However, this does not mean that these previously determined Ds (Padron-Navarta et al., 2014) are incorrect, rather that the physical process may be different. Natural olivine has the capacity (likely via Fe²⁺ oxidation, even at Mg#≈0.95) to allow H to leave the tetrahedral site (hence new OH bands), move onto a different site where faster diffusion is enabled, then rapidly exit the crystal (hence apparently fast diffusion). Numerical modelling of a combined diffusion plus reaction / inter-site redistribution process supports this suggestion. This may be the explanation for some recent studies of relative peak-specific diffusivities in natural samples, which do not match the relative diffusivities obtained experimentally.

This clearly complicates the use of H diffusion for geospeedometry – suggestions of how to recognise simple diffusion, versus diffusion plus reaction in natural samples, and how to proceed in the latter case, will be discussed.

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2.11
Formation of massive sulfide orebodies at Bor (Serbia)

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The Bor metallogenic zone contains world-class porphyry copper, high- and low-sulphidation epithermal deposits of Bor, Veliki Krivelj and a recently discovered Cukaru Peki with over 20 million tons of Cu and 1000 tons of Au (Jelenković et al., 2016). In addition to the porphyry and epithermal style veins, massive high-grade sulfide lenses are present at Bor. The massive sulfide lenses are located within the zones of advanced argillic alteration and vuggy silica. Pyrite + chalcopyrite assemblage dominating the lower part of the orebody, pyrite + pyrrhotite + chalcocite + covellite represent the main association in the central part, and enargite veinlets cross-cutting the massive sulfide ore occur predominantly in the upper part of the orebody and at the margins.

We performed leaching experiments to figure out which elements are truly immobile, and what elements are depleted and enriched in parallel to the massive sulfide formation process. The distinct change of enrichment patterns occur at the transition from the massive sulfide with residual quartz to true massive sulfide, with Cu and Au being greatly enriched in the massive sulfide sample.

Figure 1. Isocon diagrams with element concentration of mineralized samples plotted against the barren protolith (sample 67-258). Oxides are expressed in wt%, trace elements in ppm. Elements plotting above the isocon line represent gains, elements plotting below the isocon lines are losses. A. Sample BB3-23, massive sulfide with appreciable amount of residual quartz (pyrite, quartz, chalcocite, covellite and minor colusite). F. Sample BB4-48, massive sulfide (pyrite, chalcocite, covellite, minor quartz, rutile and kaolinite).

Presence of vapour inclusions in the Cu- and Au-poor core of the pyrite from the epithermal veins could indicate that vapour played significant role in the formation of earlier pyrite, but was not present in the late Cu- and Au-rich stage. One of the possible explanations for the extreme last-stage enrichment of Cu and Au is condensation of low-density Cu- and Au-enriched vapour into the aqueous fluid (Heinrich, 2005), possibly supersaturated with Cu and Au.

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2.12
A new perspective on Earth’s differentiation history from single zircon Hf isotope analysis

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The evolution of Earth’s crust-mantle system through geologic time has been investigated for many decades using various radio-isotope systems (e.g., DePaolo & Wasserburg, 1976). These studies are somewhat limited by the fact that only about 10 % of globally exposed rocks are of Archean age and most of them are difficult to access. A serious complication is that these rocks were typically affected by multiple episodes of metamorphic overprinting which makes it difficult to retrieve robust initial isotope compositions using bulk rock samples (e.g., Moorbath et al., 1997). These initial isotope ratios provide key constraints on the extent of mantle depletion and concomitant formation of granitic continental crust. In order to circumvent the problem of open-system modification of ancient rocks, many geochemical investigations conduct in-situ analysis of individual growth zones in the robust mineral zircon. That way it is possible to obtain U-Pb ages in combination with Hf isotope ratios measured on the same spot or at least same grain. Thus, the timing of rock formation and information about the differentiation of the silicate Earth can be more reliably constrained. However, all in-situ methods can only produce Hf data of modest precision, although with high spatial resolution (e.g., Fisher et al., 2011).

An alternative approach is to select individual zircon crystals without complex age zoning and determine their Hf-isotope composition by MC-ICP-MS after chemical purification of Hf. This approach enables high precision Hf isotope measurements of single crystals with uncertainties of better than 0.3 ε-units. In addition, the scatter of data is significantly less than that observed for in-situ data from individual zircon grains from the same sample. The higher resolution possible with this method is particularly relevant for early Archean samples where the differences in Hf- isotopes between the depleted mantle and crust are still very small and difficult to resolve.

This bulk method was applied to (single) zircon grains from the Archean Bastar Craton, India. The data are accompanied by previously acquired U-Pb data (LA-ICP-MS) for the temporal framework. The most primitive sample with an age of 3.59 Ga yields εHf = +1.55 ±0.22. Younger samples progressively yield more negative initial values down to εHf = -3.06 ±0.18 following a linear relationship. This data set provides firm constraints on Archean crust-mantle dynamics. While the formation of continental crust may have started early in Earth’s history, only a minor amount of enriched felsic continental crust had formed by ca. 3.6 Ga. Globally, the widespread occurrence of Archean crustal fragments with ages from 3.6-3.2 Ga may indicate the initiation of rapid and extensive growth of continental crust.

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Petrology and Medieval Indian Ocean Trade:  
Studying Amphibole-bearing Softstone Vessels and Quarries in North Eastern Madagascar

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During the Medieval Period, the North Eastern Coast of Madagascar was settled by the Islamised Rasikajy Population, who established several small towns along the coast. The archaeological record of this period yields abundant findings of local and imported ceramics, iron smelting slags and turned softstone pots, many of which were discovered in the famous cemetery site of Vohémar.

Extraction and first brute shaping of these pots was carried out in quarries in the hinterland, while the finishing most likely took place in coastal manufacturing centres. Up to now, around 20 of these quarries are known for Northern Madagascar and are being sampled systematically for this study. The aim of this study is a petrographic and geochemical characterisation of the quarries to allow subsequent provenance applications.

In the literature, the raw material used for the vessel production in Madagascar is referred to as chloriteschist, an ambiguous term considering its mineralogy and general lack of deformation. It is a mafic to ultramafic meta-cumulate, that was metasomatically metamorphosed under greenschist to amphibolite conditions and should be called Talc-Chlorite-Amphibole-Granofels by modern petrographic standards. It crops out in small 10 to 100 m scale lenses throughout the northern part of the island, seemingly independent of the respective geological units.

This rock type can be compared to an occurrence in Southern Germany, where it was first mentioned, described and named Hoesbachite after its location in the Spessart Mountains. Likewise, the softstone used in Madagascar comprises a complex assemblage of up to three generations of amphibole in a matrix of chlorite+talc+magnetite+anthophyllite+ilmenite+rutille. Due to the textural complexity and heterogeneous nature of this rock, we use a combined approach of texturally controlled microanalytics, bulk rock chemistry and optical parameters for the characterisation of the quarried localities.

Establishing a petrographical and taxonomical database of quarries and artefacts will allow the tracing of shipping routes both in Madagascar and along the Indian Ocean Trade network, as the occurrence of amphibole distinguishes this material from conventional soapstones described e.g. in Egypt and Southern Iran.
2.14
Diffusion of Ar in alkali feldspar from Shap granite (UK): fracturing of crystals and non-linear Arrhenius trajectories

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We investigate the mechanisms that drive redistribution and loss of radiogenic Ar from alkali feldspar. Several authors suggest that thermally activated volume diffusion is predominantly responsible, and that ⁴⁰Ar/³⁹Ar data obtained from this mineral by step-heating can be used to constrain the thermal histories of rocks (e.g. using multi-diffusion domain (MDD) theory; Lovera et al., 1989). Inversion of ⁴⁰Ar/³⁹Ar data to a time-temperature path is made under several assumptions, one of which is that boundaries that define diffusion domains in nature are also preserved during in vacuo step-heating. However, some researchers argue that heating of alkali feldspars results in significant textural modification, thus questioning the stability of the boundaries of diffusion domains during laboratory treatment (e.g. Parsons et al. 2010; Fitz Gerald et al., 2006). Here we attempt to identify the boundaries of diffusion domains and assess their stability by correlating Arrhenius trajectories with modifications of feldspar texture that occur in response to heating and cooling.

The problem was explored by combining two types of experiments. In vacuo repetitive step-heating experiments were used to obtain Arrhenius trajectories from fragments of alkali feldspar megacrysts from Shap granite (UK), with shortest dimension lengths of ~0.4, ~1 and ~2.2 mm. A non-linear Arrhenius trajectory from fragments with a shortest dimension length of ~0.4 mm is typical of alkali feldspars used for MDD modelling, i.e. initial (low temperature) heating steps yield higher \( \log(D/r^2) \) values than repeated isothermal steps. Non-linear Arrhenius trajectories from fragments with shortest dimension lengths of ~1 and ~2.2 mm are not suitable for MDD modelling because the initial heating steps have lower \( \log(D/r^2) \) values than repeated steps. These data suggest that at repeated isothermal steps, larger crystals yield either (i) higher diffusivities, or (ii) shorter diffusion lengths. The latter seems more feasible, given the results of heating experiments in air, which are described below.

Heating experiments in a muffle furnace in air were used to investigate modifications of feldspar texture that occur in response to heating and cooling over laboratory time scales. In addition to previously documented modification of texture, such as homogenisation of exsolution lamellae, or partial re-equilibration of K-feldspar and albite in patch perthite veins (Parsons et al. 2010; Fitz Gerald et al., 2006), we observed numerous cracks that are mostly parallel to the cleavage planes. These cracks are present both in rapidly quenched and slowly-cooled grains. They form an interconnected network and their occurrence does not always correlate with other microtextures: although mostly fracturing is more intensive around patch perthite veins, in some cases areas around them are poor in cracks.

Our results indicate that boundaries which define diffusion domains during laboratory step-heating may form during step-heating, possibly by grain fracturing. In smaller (~0.4 mm) feldspar fragments this occurred during the first heating step, while in the larger (~1 and ~2.2 mm) fragments, boundary formation occurred during several consecutive initial heating steps. Heating of feldspar crystals in air resulted in their fracturing. During step-heating of larger grains, fracturing may continue over several heating-cooling cycles. Cracks form an interconnected network, and their occurrence does not always correlate with other microtextures. These results indicate the importance of understanding the structural transformations of feldspar crystals during step-heating before using ⁴⁰Ar/³⁹Ar data for thermochronology.

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2.15

Apatite and barite preserve initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios: implications for Mesoarchean crust-mantle evolution

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Determining the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Archean rocks is quite challenging due to the high Rb/Sr ratios of most rocks that require large corrections for in-situ produced $^{87}\text{Sr}$. Added to this is the high susceptibility of Rb-Sr system to alteration. However, the minerals barite (sediments, hydrothermal deposits) and apatite (igneous rocks) generally have near zero Rb/Sr and thus corrections for the decay of $^{87}\text{Rb}$ are minimal, allowing for the direct determination of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ from individual mineral grains. Barite, formed in some Archaean marine settings, is less susceptible to later alteration than carbonates and thus is more reliable in reconstructing the isotope composition of Archaean seawater. Due to its long residence times and redox insensitivity in the oceans, Sr isotopes can be used to link the Sr-seawater trend with crustal evolution (e.g. Satkoski et al., 2017). Stratiform barites were deposited simultaneously with chromiferous chert in the ~3.3 Ga Ghattihosahalli Schist Belt, Western Dharwar Craton, India (Jayananda et al., 2008). Strong spatial heterogeneities have been preserved in Sr isotopes and major elements despite pervasive ductile deformation and regional amphibolite facies metamorphism over long time-scales. Barite grains with Rb/Sr ratios <0.003 preserve a least radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.701328±17 (2σ) that most likely records the isotope ratio at the time of formation. This low $^{87}\text{Sr}/^{86}\text{Sr}$ for seawater implies a gradual rise in $^{87}\text{Sr}/^{86}\text{Sr}$ over time rather than a steep evolution as proposed by Satkoski et al. (2016).

The initial isotopic composition of crustal igneous rocks is preserved in the accessory mineral apatite (e.g. Tsuboi and Suzuki, 2003). In situ Sr isotope measurements of single apatite grains from granitoids and metasedimentary units deposited over a time span from 3.4-2.5 Ga in the western Dharwar Craton give clear insights into the development of Archaean crust in that area. This could bring together a correlation between Sr-seawater evolution and magmatic initial Sr evolution. Rocks with igneous textures preserve pristine initial ratios in their lowest values; the more radiogenic ratios in others record recrystallization and fluid interaction. The low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in barite and some igneous apatites exclude the presence of significantly older evolved crust in the area at 3.4 Ga. This questions the nature of the crust and high net rates of continental growth during that time (Dhuime et al., 2015).

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2.16

Water retention in garnets from subducted crust, Zermatt, Switzerland

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Garnet is a common mineral in high-pressure metamorphic rocks, formed during prograde dehydration reactions at great depth (>30 km). Garnet is a nominally anhydrous mineral but it can incorporate significant amounts of water in the form of OH groups, with H substituting for cations (1-10 000 ppm H\(_2\)O; (Aines and Rossman 1984a).

The Saas-Zermatt ophiolite contains large slices of subducted high-pressure oceanic crust (2.3±0.1 Gpa, 540±20°C; (Angiboust et al. 2009). We investigated water contents in garnet from various rock types using Fourier transform infrared spectroscopy (FTIR). Samples include ultramafic rocks (Uvarovite-Andradite veins in serpentinites), mafic rocks (Meta-rodingites), and various metasediments (Garnet schists and Mn-rich metasediments). Determined water contents range from <1 for almandine garnets from metasediments to 2000 ppm H\(_2\)O for uvarovites. We set up a novel approach consisting in correlating high resolution FTIR maps with element distribution maps obtained by electron microprobe (EPMA). This method allows to determine if water incorporation and/or retention is enhanced by an element, and if H diffusion patterns are visible.

The FTIR spectra display different bands according to the composition of the garnet, showing that H incorporated in garnet is strongly influenced by nearest neighbours. Correlation of FTIR and EPMA maps reveal high correlation between chemical zoning and water zoning. Some garnet compositions are thus more likely to retain/incorporate water: Ca\(^{2+}\) - Cr\(^{3+}/Fe^{3+}\) garnets > Ca\(^{2+}\)-Al\(^{3+}\) garnets> Mn\(^{2+}\)-Al\(^{3+}\) garnets >>> Fe\(^{2+}\)-Mg\(^{2+}\)-Al\(^{3+}\) garnets. Most of the garnets preserve water zoning acquired during prograde growth and show little evidences of H diffusional loss during their exhumation back to the surface.

Rock types containing garnet with high water contents represent a small volume in the oceanic crust, and therefore represent a minor contribution to the water budget in subduction zones. Nonetheless, due to the large P-T stability field of garnet, any water incorporated in the crystal structure might be transported to deeper parts of the mantle, after the breakdown of hydrous phases.

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2.17
Comparative study of XRF and portable XRF analysis and application in hydrothermal alteration geochemistry: The Elatsite porphyry Cu-Au-PGE deposit, Bulgaria

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X-ray fluorescence (XRF) spectrometry is a non-destructive analytical technique widely used in Earth and Environmental Sciences to determine the elemental composition of rocks, ores, soils and plants. Portable XRF analysers (pXRF) are increasingly being used in mineral exploration and mining, allowing acquiring rapidly and inexpensively large geochemical data sets in the field. In this contribution, we present the results of a comparative study of 15 samples of hydrothermally altered magmatic and metamorphic rocks from the Elatsite porphyry Cu-Au-PGE deposit in Bulgaria, using both a lab-based WD-XRF (PANalytical AxiosmAX) and a pXRF (Thermo Niton XL3t) device.

For analyses performed with the pXRF, the samples were crushed to a fine-grained powder (<80 μm) and mounted in a plastic cup covered by a thin polypropylene film (4 μm-thick) to be analysed on a test stand. Two techniques for sample preparation were used, resulting in slight difference in compaction of the sample measured: the first one consists of analysis of non-pressed powder in the cup (referred to as “powder” in Fig. 1), and in the second case the powder is slightly compressed with an agate pestle (referred to as “pressed powder” in Fig.1). A total of 34 elements were measured using the “Soils & Minerals” protocol within the “Mining Cu/Zn” mode of the pXRF. Measurements were 120s each consisting of two 60s cycles using four different energy filters. For some elements (Al, V, Mn, Mo, Ba) pressed-powder samples show systematically slightly higher values (as high as 10%; Fig. 1C).

Lab-based WD-XRF results were used to perform an empirical calibration of the elemental concentrations obtained by pXRF, following the procedure proposed by Mauriohooho et al. (2016) (Fig. 1A-B). Linear regression analysis of the data allows calculating the correction factor to be applied (corresponding to the slope of the regression line) for each element determined by pXRF. For each filter, the correction factor decreases progressively with the increase of the atomic number of the measured element (Fig. 1D).

Comparing the results obtained using the two sample preparation techniques for the pXRF analyses, we demonstrate that generally both of them provide accurate data comparable with WD-XRF (Fig. 1B), resulting in correlation coefficients >0.9. However for some elements (ex. Al, Sr, Zn), pressed-powder preparation resulted in better correlation between WD-XRF and pXRF analyses.

Unfortunately, due to its low atomic number, Na cannot be quantified by pXRF, and Mg is usually measured with a low level of confidence.

Our results demonstrate that large data sets obtained with a pXRF device can be used after correction based on lab-XRF analyses on selected representative samples for geochemical interpretation on suites of hydrothermally altered samples (mass balance and alteration index calculations).
Figure 1. Comparison between lab-based WD-XRF and pXRF analyses of hydrothermally altered rock samples: A) K concentrations of powder and pressed-powder samples vs. lab-XRF analyses; calculated slopes from regression analysis are used as correction coefficients; B) Corrected values of K concentrations from pXRF analyses vs. lab-XRF data; C) Powder vs. pressed-powder sample preparation for pXRF analyses (Al concentrations); D) Correction factor as a function of Z (atomic number) of the elements for the four different filters used (light, low, main, high).

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2.18
Fluid-rock interaction in subduction zones: an integrated thermodynamic and $\delta^{18}$O fractionation modelling approach

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Oxygen stable isotopes are important tools for a wide range of applications in Earth sciences as the oxygen isotopic signature of minerals records the physical and chemical conditions of equilibration. Oxygen isotope fractionation between minerals has been widely used for thermometry, but also to investigate samples that experienced fluid-rock interactions. The petrological interpretation of oxygen isotope data requires the knowledge of the fractionation behaviour between two phases and its evolution with temperature. A few well-documented compilations of fractionation factors are available in the literature, but they are either restricted to small chemical systems or based on different methods, making the data not consistent with each other. In this study, we report the first internally consistent database for oxygen fractionation that includes fractionation factors for most major and accessory phases and a pure $H_2O$ fluid phase. This database has been derived simultaneously using a least square regression technique based on a large dataset of published experimental, theoretical and natural data. All the constraints for a given phase contributed to the refinement of its fractionation properties, making the final database internally consistent.

This database can be applied in a general thermodynamic framework to model the evolution of $\delta^{18}$O in minerals through their metamorphic history. For a given bulk rock composition, the evolution of the mineral assemblages, modes and compositions can be predicted along any P-T path using Gibbs free energy minimization. If the $\delta^{18}$O of one phase is known, it is possible to recalculate the $\delta^{18}$O of the other phases in equilibrium as well as the bulk $\delta^{18}$O. If the bulk $\delta^{18}$O is known, the $\delta^{18}$O values of each phase at any given P-T can be predicted and compared with natural data from mineral and mineral zone analyses. This modelling strategy enhances our ability to investigate samples that experienced complex thermal histories and/or fluid-rock interactions. It also provides a strong theoretical basis for evaluating to what extend a rock has evolved either as an open system with respect to oxygen isotopes, or as a closed system fully or partially re-equilibrated.

This approach was applied to investigate the metamorphic and metasomatic evolution of high-pressure (HP) rocks from the Sesia Zone in the Western Alps. These accreted continental fragments consist of poly-metamorphic and mono-metamorphic lithotypes such as metagranitoids, metasediments, and mafic boudins that recorded different pre-Alpine histories and different P-T-t paths during the Alpine orogenic cycle. Several lines of evidence support the presence of fluids at HP conditions. In situ $\delta^{18}$O analysis allows the isotopic composition of mineral zones to be resolved and related to mineral textures reconcilable with growth zoning, but also resorption and replacement processes. The $\delta^{18}$O values of different garnet zones, in combination with petrological modelling, can assist in identifying episodes of external versus internal fluid fluxes. Relics of pre-Alpine garnet in different metasediments from the Eclogitic Micaschist Complex show systematically higher $\delta^{18}$O values with respect to Alpine rims, suggesting a significant input of external fluids between the Permian high-temperature stage and the HP Alpine metamorphism. The oxygen isotope fractionation modelling is critical to reconstruct fluid sources and pathways through the crust during subduction.
Figure 1. Representative garnet grain from the Eclogitic Micaschist Complex. Pre-Alpine core and Alpine rim are visible in the chemical map. The location of the SIMS analysis (circles) and the corresponding $\delta^{18}$O value in ‰ are reported. Core and rim $\delta^{18}$O compositions differ by ~4 ‰.
In-situ garnet $^{238}\text{U}-^{230}\text{Th}$ geochronology of Holocene silica-undersaturated volcanic tuffs at millennial-scale precision

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Accurate geochronology of Quaternary silica-undersaturated alkaline volcanic rocks is notoriously difficult. This is because K-rich minerals from these type of rocks commonly contain significant amounts of excess-40Ar, rendering 40Ar/39Ar dates unreliable. This significantly limits our ability to assess the frequency of eruptions in alkaline volcanic provinces, evaluate related volcanic risk and date associated archaeological sites. Here, we present a new approach to dating alkaline volcanic rocks employing $^{238}\text{U}-^{230}\text{Th}$ disequilibrium dating of Ca-rich garnet phenocrysts by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). We document analytical protocols and apply this technique to date magmatic garnets from historic eruptions of the Somma-Vesuvius volcanic complex (Southern Italy) and from the Engare Sero Footprint Tuff, a volcaniclastic unit attributed to Oldoinyo Lengai (Northern Tanzania) that contains abundant Hominin footprints (Balashova et al., 2016; Liutkus-Pierce et al., 2017). Garnet phenocrysts from historic eruptions of Vesuvius yield well-defined U-Th isochrons with crystallization ages indistinguishable from known eruption ages suggesting that garnet crystallized close to eruption with short pre-eruption residence times. Garnets from the Engare Sero Footprint Tuff yield a U-Th isochron with an age of 4.91 ± 0.58 ka. This date is compatible with $^{14}$C and 40Ar/39Ar dates that bracket tuff deposition to between ~5 and ~19 ka (Liutkus-Pierce et al., 2017) but confidently constrains the age of the Engare Sero Footprint Tuff to the mid-Holocene. These examples demonstrate the potential of this new approach for dating Late Pleistocene to Holocene silica undersaturated volcanic rocks at millennial-scale precision and for investigating magma chamber processes beneath active alkaline volcanoes.

REFERENCES


**P 2.1**

**Advances in geological microanalysis: Correlation and Machine Learning**

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Techniques such as Light Microscopy (LM), Scanning Electron Microscopy (SEM), Automated Mineralogy (AM) and Laser-Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) are often viewed in isolation; there has been limited functional development on the correlation and integration of these techniques to advance geological microanalysis. This is required, as geological structures are highly heterogeneous, and so the resolution required to image fundamental microstructures frequently comes at the expense of a field of view representative of that heterogeneity. Even more critically, no single tool gives complete information about the sample, and frequently analyses are complementary. In this paper we will show how these techniques can be integrated together using machine learning and advanced data science to generate unique insights into the geological processes in question, with specific application to multiscale characterization of shales and understanding mineralogical characterization of hydrothermal vents.

Unconventional reservoirs have transformed the energy industry, but a detailed understanding of their structure and flow behavior at the micro and nano scale remains a challenge. Reservoir rocks exhibit strong structural heterogeneities spanning length scales ranging from the km down to the nm or even sub-nm scale (Ringrose, Martinius and Alvestad, 2008). An understanding of mineralogy is critical to understand reservoir flow behavior and geomechanical response (Oliver et al., 2016;2015; Ashton et al., 2013; Ganguly and Cipolla, 2012). Recent developments in high throughput automated digital petrography digitization allow for entire thin sections to be fully digitized in a matter of minutes. Local microfacies can then be identified using machine learning based image classification. These locations can then be used as the targets for high resolution Automated Mineralogy analyses through a common (sample centric) control system. By maintaining the relationship between local microstructure and macroscopic heterogeneity, data can directly upscaled to the pore to core scale.

One of the principal challenges associated with detailed microanalysis is that of data scale and analysis. With the advent of high throughput, automated mapping technologies, we need equally powerful analytical tools to allow for the interpretation of the resulting data. The last 10 years have seen a transformation in a broad group of technologies frequently grouped together as “machine learning”. By integrating and spatially registering disparate datasets acquired on different tools, and feeding the resulting data into a machine learning algorithm (Breiman, 2001), it is possible to automatically classify mineralogical variations over extremely large areas at high resolution extremely rapidly (figure 2).
Figure 2. Automated mineralogy overlay of type 1 and type 2 magnetite, imaged using high throughput automated digital petrography, then used to locate regions for LA-ICP-MS analyses.

When applied to subsurface hydrothermal vent samples, this analysis reveals the spatial variation of Chalcopyrite-Bornite alteration, governed by the variation of (and heterogeneity in) fluid flow fields within the vent. This is true both in the center of the central vent flow pathway, where flow and alteration is concentrated, but also within the vent matrix, where flow appears to be strongly concentrated in targeted banded regions.

REFERENCES
P 2.2
Mineralization and fluid inclusion investigations of the Miocene sandstone hosted fluorite ore deposits, Northeastern Tunisia

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The fluorite-bearing Miocene mineralizations of the Oued M’Tak (Northeastern Tunisia) (Fig. 1) are hosted in either glauconitic sandstone units of the Mahmoud Formation (Miocene: Upper Langhian) and the lower part and bioclastic limestone of Aïn Grab Formation (Miocene: Middle Langhian).
Field studies show clearly the same depositing mechanism for mineralization outcropping in the different areas in Oued M’Tak.
Mineralization shows different textures: massive, geodic and disseminate. The fluorite is locally accompanied with sphalerite, quartz, and calcite. Cavities are filled by idiomorphic, cubic, zoned fluorite crystals, minor idiomorphic calcite scalenoedrons and extremely rare crystals of sphalerite.
Fluid inclusions in fluorite are characterised by homogenization temperature (Th) between 110°C and 160°C and salinities values ranging from 14 wt % equiv. NaCl to 20 wt % equiv. NaCl. The gaseous fluid inclusions show ice-melting temperature (Tmi (gas) <-56.6 to -60°C) that reveals the presence pure CO₂ with a small quantity of CH₄.
This mineralization is similar to that of the main Tunisian fluorite deposits.
Mineralogy and microthermoetry studies indicate that the mineralization results from a mixture of two aqueous fluids characterized by different temperatures and different salinities. The fluorite deposits are plausibly post Miocene in age and classified in the MVT-Type-class.

Figure 1. Map showing the Oued M’Tak fluorite deposit, in north-eastern Tunisia (Bejaoui et al., 2013).

REFERENCES
P 2.3
Sr isotope geochemistry of the Bor Cu-Au system: Is Late Cretaceous seawater involved in magmatic-hydrothermal ore formation?

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Bor is a mine site in Eastern Serbia located in the Late Cretaceous subduction-related andesitic Timok Magmatic Complex (TMC). The Bor Cu-Au deposit hosts economically important amounts of copper and gold, disseminated in several ore bodies with unequal ore grades. In this study two genetically linked ore bodies have been selected, Borska reka, a porphyry ore body and T ore body, a high-sulfidation epithermal ore body, for the extraction of anhydrite from veins. A Rb-Sr isotope dilution approach was used to determine the fluid sources by comparing the $^{87}$Sr/$^{86}$Sr ratios of anhydrite on different levels with magmatic whole rock samples, Late Cretaceous seawater and basement whole rock samples. The findings are indicating a close genetic relation of the porphyry part (0.702850 – 0.705889) to primitive magmatic rocks of the TMC (0.703493 – 0.705284) and therefore to magmatic fluids. The range of scatter displays homogeneous to inhomogeneous assimilation of andesitic host rock and minor contamination in a late stage of formation in the upper transitional part of the porphyry system. The scattering of the Sr isotope data of the porphyry part is probably primary. The high-sulfidation epithermal part of the system (0.705331 – 0.706123) shows an overall trend to lay slightly above the primitive magmatic rocks and the scatter cannot be explained by simply inhomogeneous assimilation of andesitic host rock. The scattering in the epithermal part is mainly secondary and caused by mixing of fluids derived from magmatic water and fluids derived from an additional source. Vein cross profiles indicate a coherent trend, without greater perturbation, of increasing $^{87}$Sr/$^{86}$Sr ratios towards the internal part of the veins and towards the top part of the deposit. This trend could indicate that the contribution of the contaminating fluid was more evolved in the shallow part of the porphyry-high-sulfidation epithermal system. From the findings influence of seawater to the porphyry-high-sulfidation epithermal system in a late stage of formation is a likely scenario.
U/Pb zircon dating of Miocene magmatism in the Apuseni Mountains (Romania) and time relationship of intrusive events at the Certej Deposit

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The Southern Apuseni Mountains (SAM) in the Inner Carpathians of Romania are hosting some of Europe’s biggest porphyry Cu-Au and epithermal Au-Ag deposits. The source magmas of these deposits are Miocene in age and calc-alkaline in composition. Most of the magmatic rocks in the SAM crop out along two graben-like structures that are oriented NW-SE. Based on the K/Ar method, their emplacement was dated to between 14.7 and 7.4 Ma (Roșu et al., 2004). Being situated about 200 km away from the East Carpathian volcanic arc, active subduction in the Miocene can be excluded. Harris et al. (2013) therefore suggest decompression melting of a previous metasomatized mantle and later asthenosphere upwelling to be the reason for the found magmatic suite.

The Certej project is an epithermal Au-Ag deposit and is situated in the South of the SAM inside the NW-SE orientated Brad-Zlatna basin. The mineralization occurred along the contact of three porphyritic andesite intrusions and the Cretaceous and Neogene basin sediments.

Four sample positions of Roșu et al. (2004) have been redated using the LA-ICP-MS U/Pb dating method on zircons. Drill-core sections of several intrusive bodies at the Certej project were analyzed with the same method. To narrow down the magmatic activity at the mine site, three main intrusions were dated with ID-TIMS and revealed a lifetime of approximately 75'000 years.

Zircon chemistry (REE, Eu/Eu* and Hf) in addition to bulk rock XRF data of eight regional samples and literature data show a trend towards an increasing mantle influence over time in the SAM. It is therefore proposed, that the heterogeneous magma sources could be the product of mixing processes of crustal contaminated early melts with later lithospheric derived melts.

REFERENCES
Porphyry-style alteration and vein types of the Far Southeast porphyry Cu-Au deposit, Mankanyan District, Philippines

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Ninety-six underground diamond holes (~102 km) drilled by Far Southeast Gold Resources at the Far Southeast Cu-Au porphyry deposit provides a 3-dimensional exposure of the deposit between 700 and -750m elevations; surface at ~1400m elevation. Drill holes intersect the base of advanced argillic-silicic alteration that hosts the supra-adjacent Lepanto high-sulfidation mineralization, the top of the porphyry deposit as defined by stockwork veins, the main ore body and an underlying subeconomic zone. The 1% Cu equivalent ore shell is mainly located at 500 to -300m elevation.

Alteration assemblages were determined by drill core logging, SWIR (Short Wavelength Infra-Red) spectral analysis, and a petrographic study. Alteration is zoned around veins, or pervasive where zoned assemblages coalesce. Mineral sequence includes early granular grey/white quartz-rich veins with potassic alteration (biotite-magnetite-K-feldspar), followed by euhedral lavender quartz-rich veins (color resulting from the presence of hematite daughter minerals in fluid inclusions) with SCA alteration (sericite-chlorite-albite) – associated with the bulk of Cu deposition as chalcopyrite and bornite – and late anhydrite-rich veins with phyllic alteration (illite-muscovite-pyrite). Thin Cu-sulfide rich veins (‘paint’ veins) are associated with SCA alteration. Timing between veins is recorded by crosscutting and reopening textures whereas timing of alteration is recorded in overprinting of assemblages, and a change in mineral composition (e.g., albitization of plagioclase affected by SCA alteration).

Shallow advanced argillic mineral assemblages (pyrophyllite-diaspore-alunite-kaolinite) overlie SCA alteration and deep potassic alteration. It is also found at depth, mainly along structures. Illite crystallinity variations recorded by SWIR implies higher temperature of formation with decreasing distance to high grade zones.

Variations in alteration mineralogy are a consequence of a change in temperature and fluid composition of the hydrothermal fluids. Cross-cutting relations that contradict general observations of timing are the result of multiple pulses of hydrothermal fluid that overprinted one another.
Holuhraun-Bardarbunga 2014-2015 (Iceland) eruption: reconstructing deep magma dynamics with cluster analysis

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Petrography and geochemistry of eruptive products are commonly used to reconstruct magmatic processes occurring at depth and preceding volcanic eruptions. While this approach is central to our understanding of processes occurring at inaccessible depths, analyses and sample preparation are time consuming, which limits the number of samples that can be analysed. This, in turn, hinders the possibility to rank the relative importance of processes on a statistically significant way. We collected samples of the Holuhraun-Bardarbunga eruption, emitted from September 2014 to February 2015 and collected 60 core-to-rim profiles electron microprobe profiles of chemically zoned clinopyroxenes. The analyses were treated using dimensionality reduction and clustering algorithms. This approach allowed us to identify clusters of clinopyroxene zone chemistry, quantify their relative abundances and establish the relative sequence of their appearance in the clinopyroxene profiles (i.e. relative temporal sequence).

The results show that two different magmas were injected at the base of the crust in different proportions (83 vs 7%). Most of these magmas mixed at depth before being transferred at shallow depth and erupted (95%), while the remaining 5% bypassed any intermediate reservoir, were transported at shallow depth and erupted. Variations to this general picture were observed during the eruption that we are currently linking to geophysical observations collected during the eruption (Sigmundsson et al., 2014; Gudmundsson et al., 2016).

Our findings are in line with recently published melt inclusion studies (Bali et al., 2018, Hartley et al., 2018), allow for quantitative assessment of the relative importance of magmatic processes at depth and suggest our approach can provide a frame and be used to target high precision geochemical studies.

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P 2.7

Rapid, distinct magma generation preceding four caldera-forming eruptions in the Southern Rocky Mountain Volcanic Field

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The Southern Rocky Mountain Volcanic Field (SRMVF) is an exceptional expression of the widespread mid-Cenozoic ignimbrite flare-up in western North America. Within the SRMVF, which is over 1000 km inland of the western edge of North America, the nine caldera-forming eruptions of the central caldera cluster in the San Juan Mountains produced over 8000 km³ of explosive volcanic rock in less than two million years (28.7 - 26.87 Ma). The last 40 k.y. of this central caldera cycle produced over 1400 km³ of material during four caldera-forming eruptions, the Rat Creek Tuff (RCT), Cebolla Creek Tuff (CCT), Nelson Mountain Tuff (NMT), and Snowshoe Mountain Tuff (SMT), from oldest to youngest. The RCT and NMT are zoned in composition (dacite to rhyolite) and crystallinity (~5-35 vol%), and the CCT and SMT are crystal-rich (20-35 vol%) and unzoned (dacite). These rapid, sequential eruptions make this an excellent natural laboratory for studying extremely productive magmatic systems. We present petrographic thin section analyses in addition to whole-rock, glass, and mineral major and trace element data to determine 1) genetic links, if any exist, between these eruptions and 2) magmatic reservoir conditions preceding these eruptions. Whole-rock major and trace element patterns imply a common magma generation process in a subduction setting for all four eruptions. Petrography and geochemical data suggest that whereas the zoned and unzoned ignimbrites share some similarities, the pre-eruptive evolution and storage conditions are specific to each eruption. Our results confirm that the thermal, chemical, and physical architecture of large magma reservoirs is complex, leading to the release of magmas with distinct properties in a short period. Such complex magmatic systems call for a revision of models regarding the triggering of large eruptions and a reassessment of the interpretation of geophysical signs of unrest in large, active volcanic systems.
Do U-Pb zircon dates from residual melts in mafic magmatic systems record protracted crystallization?

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Zircon is found rather commonly in mafic rocks from large igneous provinces (LIP) despite their high crystallization temperatures and low zirconium contents, which apparently contradicts zircon saturation conditions. However, zircon grains in these rocks occur as tiny crystals in pockets of highly evolved melt that crystallize at much lower temperatures than the bulk of the magma and that contains high concentrations of incompatible elements. Consequently, such zircon contains variable and high trace element concentrations. As a consequence, zircon U-Pb ages from mafic rocks are expected to record uniform ages at around the ± 0.02% uncertainty level (once the effects of Pb loss have been removed) and have been instrumental in determining precise and accurate ages for many of the Phanerozoic large igneous provinces.

Here we report zircon U-Pb ages from 2 samples from the North Mountain basalt (Bay of Fundy, Canada), one of the earliest eruptions from the Central Atlantic magmatic province (CAMP) that range in age from ~204 Ma to ~201.5 Ma. This age range is significantly longer than what we would expect from typical LIP zircon. CL images of a large suite of these zircon crystals do not contain evidence for xenocrystic cores, also Hf isotope data do not suggest crustal contamination. Simple mass balance calculations suggest that only tiny xenocrystic cores of ~600 Ma (the age mode of zircon from the sediments through which the North Mountain basalt is emplaced) would be required to explain the oldest ages, although these have not been discovered in the CL imaging. Alternatively, the old ages could reflect early magmatic activity associated with the CAMP, which implies (i) that this presumably mafic early magmatism would have to produce zircon with low U, which is a characteristic of the >201.5 Ma grains, and (ii) that these grains would then have to survive transport in a zircon under-saturated mafic melt to the surface, which seems rather unlikely.

In any case, this study highlights the fact that zircon U-Pb data from LIP magmas can be as complicated to interpret as those from more felsic systems.
P 2.9
Water in orthopyroxene: orientation and thickness calibration using FTIR: from the lab to natural samples

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Hydroxyl (colloquially referred to as water) located in crystalline defects of Nominally Anhydrous Minerals (NAMs) can represent a few to hundreds of parts per million (ppm) H₂O. This is enough to affect the phase equilibria and rheological properties of the mantle, and makes NAMs a significant contributor to the total mantle water budget. Fourier Transform Infrared Spectroscopy (FTIR) absorption peak locations in the OH stretching region are related to the local crystallographic environment of the OH chemical bonds in the mineral and can be used to calculate water content. Orthopyroxene, being the second most important phase of the upper mantle, has a greater water storage capacity compared to olivine, making it the dominant host of water in the upper mantle. However, even if many studies have quantified the water content in orthopyroxenes, the hydrogen incorporation and diffusion mechanisms are still not very well constrained. Orthopyroxene is an anisotropic, orthorhombic mineral with two perfect cleavages. In natural samples, the orientation of the crystals may be unknown and the thickness may slightly vary between crystals, which affects FTIR measurements, and thus, water concentration calculations and potentially hydrogen diffusion profiles. This study presents a way of minimizing these uncertainties on orthopyroxenes using calibration coefficients to correct for thickness and orientation using only the information measured by FTIR without any external measurements required.

This is done using the Si-O overtones, located between wavenumbers 1530 and 2250 cm⁻¹ (figure 1). For the thickness correction, a series FTIR measurements were made on 12 orthopyroxene grains, where 30 to 50 microns were removed at each step. A linear regression (forced through the origin) was calculated for three distinct populations and shows that the thickness correction coefficient is orientation dependent (figure 1). Therefore, an orientation determination is calculated using the method of Asimow et al. (2006) adapted for orthopyroxene, allowing the dominant orientation to be determined, and its influence on the Si-O overtones and the water contents. The orientation correction is calculated using the polarization vector of the unoriented sample and by comparing it to the three main axis spectra (a, b and c). These corrections are applied on orthopyroxene from natural backarc-peridotite samples derived from several localities in Southern Patagonia.
Figure 1: A) Close-up of the Si-O overtones unpolarized FTIR measurements, showing 3 main groups with different orientations. B) The integrated area of the Si-O overtones plotted against different thicknesses show the 3 groups with the 3 different line fitting equations, showing the orientation-dependance of the results.

REFERENCE
P 2.10
Architecture of a distal skarn system: Calamita Fe-skarn deposit, Elba Island, Italy

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The Messinian Fe-ore deposits of the Elba Island (Italy) form a narrow N-S belt along the eastern coast of the Island and have been exploited since the 1st Millenium BC until the 1980’s (Tanelli et al., 2001; Dünkel, 2002). Most of them are spatially and genetically associated with distal skarn bodies showing no direct relationship with causative intrusions.

The collapse of the Apenninic orogen, took place during the Oligocene-Miocene and generated the opening of the Tyrrhenian Basin (Keller & Pialli, 1990). As a consequence of the extension, felsic peraluminous magmas were emplaced at shallow crustal levels. This magmatism created the Tuscan Magmatic Province, which affected the central-west part of Italy, including the Elba Island as well (Dini et al., 2002). The granitoids on Elba are emplaced within previously metamorphosed lithologies, dominated by schists, gneisses and marbles. Skarn bodies hosting the Fe-ores on Elba are distal to the large granitic intrusions and the genetic connection with the intrusive magmatism is still debated.

The Calamita Fe-skarn is located in the southernmost part of the mineralized belt. The deposit displays a remarkable N-S zonation and consists of partially interconnected, multi-layered skarn bodies variably associated with magnetite-hematite ores, hosted by dominantly carbonate formations overlaying an extensional fault zone that separates them from the underlying micaschists of the Mt. Calamita Complex. The northern sector of the deposit consists of a garnet (andradite)-dominated skarn, with minor hedenbergite, ilvaite and sulphides (pyrite and chalcopyrite) to the west and a hedenbergite-ilvaite zone to the east. The two zones display a complex gradual contact most probably inheriting former lithological boundaries. The central sector of the deposit is dominated by a hedenbergite-ilvaite skarn, with minor lense-like bodies of garnet-hedenbergite skarn. The southern sector, close to the coast line, consists of a hedenbergite-ilvaite skarn only, with ilvaite being the major mineral in the southernmost outcrops. The lower contact of the skarn with the host Calamita micaschists is extensively epidotized and frequently displays pyrite disseminations and abundant tiny adularia-epidote-amphibole veins. Due to erosion, the host rocks at the upper contact of the deposit have never been observed.

The major skarn silicates at Calamita – hedenbergite, ilvaite and garnet – commonly form massive textures (typical for the garnet zone), complex intergrowth (garnet-hedenbergite, hedenbergite-ilvaite) textures, indicative of co-precipitation, or banded strongly folded textures with prominent zonation (ex., hedenbergite-ilvaite), reflecting selective replacement along foliation planes of the marble precursor and/or cyclic changes of physical and chemical parameters of the skarn-forming fluids. Textural, AMS, mineral chemistry (major and trace elements) and fluid inclusion analyses of skarn silicates are in progress in order to study the skarn-forming processes at Calamita and eventually to establish geochemical and mineral vectors towards causative magmatic bodies.

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Tracing Sn and W pre-concentrations in the Limousin ophiolite and Variscan granites

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The French Massif Central (FMC) is part of the West European Variscan belt, which was formed during the Devonian continent-continent collision between the Gondwana and Baltica, following the closure of oceanic domains opened during the Cambrian-Ordovician and collision of Gondwana-derived continental fragments (Eo-Variscan stage; Silurian-Devonian) (e.g. von Raumer et al., 2015). The FMC is composed of a series of nappes that were piled during the Meso-Variscan period (Devonian-Early Carboniferous; c. 350–360 Ma) (Ledru et al., 1994). The Neo-Variscan stage (Late Carboniferous-Early Permian) corresponds to extensive granitic magmatism and formation of major crustal-scale shear zones. The FMC hosts numerous Variscan ore deposits, some of them being known since the gallo-roman times (e.g. Au). In particular, the FMC contains economic to sub-economic deposits of W and Sn, which were formed during the late stage of uplift (320–290 Ma) (e.g. Marignac and Cuney, 1999; Alexandrov et al., 2000). Most of the W–Sn deposits are hosted by metasediments, while minor W–Sn deposits are hosted by rare metal peraluminous granites (RMG) found in the Northern Limousin (Marignac and Cuney 1999; Vallance et al., 2001). Mineralised structures in the Limousin are vein-hosted and arise from percolation of different hydrothermal fluids related to: 1) the delamination of the lower lithosphere during exhumation of the Variscan belt and, 2) granulite-facies metamorphism at the basis of the lower crust (Vallance et al., 2001; Harlaux et al., 2017). Frequently, metal associations are complex and reflect different source rocks: Au (As, Bi, Sb, Te) W–Sn (Nb, Ta, REE).

We have analysed compatible and incompatible metallic trace elements in the mineral assemblage of a series of rocks from the Limousin ophiolite (serpentinites, amphibolite facies metagabbros and basic dykes) and felsic magmatic series (granites as well as gneisses) (Vaulry W–Sn district; St Yrieix, Cheni and Lauriéras Au districts; St-Sylvestre and La Marche U districts). Determination of the trace element concentrations in non-mineralised rocks is expected to trace the source of Sn and W transported by fluids involved in the formation of Variscan ore deposits.

In the Limousin ophiolite, serpentinites and amphibolites have Sn concentration below the determination limit (<0.25 ppm) and low abundances of W (0.3–1.8 ppm), which differs from the high abundances measured for compatible transition metals (i.e. Sc, V, Cr, Co, Ni, Zn, Cu). In serpentinites, minerals (serpentine, olivine, amphibole, chlorite and spinel) generally display low contents of Sn and W (0.2–5.8 and 0.2–7.6 ppm, respectively). In amphibolites, amphibole has low Sn and W contents (Sn: 0.2–1.2 ppm; W: below detection limit), while higher concentrations are measured in accessory titanite (Sn: 4.7–5.6 ppm, W: 16–18 ppm). W and Sn concentrations are generally below detection limit (<1.2 ppm) in plagioclase. By contrast, high concentrations of Sn and W (0.51 and 14 ppm, respectively) are found in hydrothermal fluids related to: 1) the delamination of the lower lithosphere during exhumation of the Variscan belt and, 2) granulite-facies metamorphism at the basis of the lower crust (Vallance et al., 2001; Harlaux et al., 2017). Frequently, metal associations are complex and reflect different source rocks: Au (As, Bi, Sb, Te) W–Sn (Nb, Ta, REE).

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Our results argue for a local source of W and Sn pre-concentrations, in agreement with Vallance et al. (2001), who has considered the Blond granite as the main source for mineralisation in the Vaulry major W–Sn district. There is no evidence of Sn and W mobilisation from the surrounding rocks. Subsequent percolation of hot pseudo-metamorphic fluids is thought to have leached W and Sn from the granite, and triggered precipitation of W- and Sn-rich minerals (wolframite, scheelite,
cassiterite) in hydrothermal veins (Vallance et al., 2001). By analogy, the St Sylvestre and La Marche leucogranites may be the local source for the minor W–Sn deposits hosted in the two districts while specific element association may be derived locally from some basic lithologies.

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P 2.12
The Sakdrisi Au-Cu deposit, Bolnisi mining district, Georgia: providing a genetic model based on petrographic, geochemical, structural, and alteration studies.

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The Late Cretaceous Sakdrisi epithermal Au(-Cu) deposit is located in southern Georgia, 50 km southwest from the capital Tbilisi, in the Bolnisi mining district. The area is located at the transition between the Eastern Pontides to the West and the Lesser Caucasus to the East, both resulting from the convergence of the African-Arabian plates and the European margin, during the N-NE verging subduction and closure of the northern branch of the Neotethys. The mineralization is hosted by a Late Cretaceous bimodal sequence of volcanic and volcano-sedimentary rocks. The deposit is poorly constrained, and the aim of this work is to perform a comprehensive geological, petrographic, alteration and geochemical study to provide a new genetic model. Our preliminary working model is presented in Figure 1.

Sakdrisi consists of a 2-km long cluster of five mineralized centers aligned along a NE-oriented fault zone. The western part of the fault is covered by a barren ignimbrite, crosscut by andesitic and basaltic dikes, while the eastern side mainly consists of andesitic to dacitic volcanic rocks and tuff. Two distinct types of ore are currently exploited in this mine: 1) auriferous quartz-barite and quartz-chalcedony veins surrounded by illite-siderite alteration haloes, in the brecciated silicified and oxidized volcaniclastic rocks of Sakdrisi’s lithocap; and 2) a more reduced zone hosting a stockwork of subvertical chalcopyrite-rich quartz-amethyst and quartz-carbonate veins. The latter most certainly represents the deeper parts of the system, and is directly overlain by the lithocap, which has undergone supergene enrichment, suggested by the occurrence of minerals like chalcocite. At the bottom of open pit V (May 2018), gold grade is estimated @1ppm, at a cutoff grade of 0.2 ppm. At the Sakdrisi open pit IV, the grade is 1.6 ppm. Copper is a by-product, and the average grades are 0.12 wt.% at Sakdrisi IV and 0.5 wt.% at Sakdrisi V.

The mineralized host rocks of open pit IV have been overthrusted by a barren ignimbrite, preserving the ore from erosion. A set of NW oriented secondary faults could explain why a supergene enrichment zone was preserved in open pit V, but was eroded in the remaining uplifted blocks. Silification of the host rocks was reported down to a depth of 100-150m below the surface, while epidote and sericite have been described down to 200m below surface in previous studies. Argillic (illite-montmorillonite) and carbonate (ankerite) alterations are very common.

Transmitted and reflected light petrographic studies, together with Raman, XRD and XRF analyses will be performed, in order to define the chronology of mineralizing events and related hydrothermal alteration. U-Pb dating on dike-like structures crosscutting the ore bodies will allow us to constrain the timing of mineralization, as well as 40Ar/39Ar dating on adularia, if present. Spatial (vertical) and temporal physico-chemical evolution of the mineralizing fluids (T°, composition) will be constrained by fluid inclusion petrography and microthermometry analyses on idiomorphic quartz crystals collected at different levels of the open pits. The origin of these fluids will be investigated by stable isotope geochemistry on micas and clay minerals (δ18O, δD) and on sulfides and sulfates, including barite (δ34S). The dataset will be combined with ore grade distribution provided by the mine staff in order to propose a synthetic genetic and exploration model for Sakdrisi.
Figure 1 – Preliminary genetic model for the Sakdrisi epithermal deposit with a sequence of events from oldest at the top to youngest at the bottom.
Temporal and geochemical characterization of the Tejsar magmatic complex, northern Armenia, Lesser Caucasus

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The Tejsar magmatic complex is located in the Lesser Caucasus and belongs to the northern part of the South Armenian block along the Amašia-Sevan-Akera suture zone. It consists of a wide range of Cenozoic magmatic rocks emplaced during the convergence of the Arabian plate toward the Eurasian margin, as the result of the Neotethys ocean closure. Dextral strike-slip tectonics along the South Armenian Block result from the oblique plate convergence, which in turn controlled both the magma ascent in the upper crust and the emplacement of associated ore deposits (Hovakimyan et al., in review). The geologic evolution of the Lesser Caucasus remains unclear, therefore constraining the petrography, geochemistry and geochronology of the Tejsar complex will provide new insights in the understanding of the regional geodynamic evolution. The study area includes a large set of magmatic rocks varying from mafic intrusions and lavas to more differentiated rocks (e.g. nepheline syenite). Although the different magmatic rocks have a distinct mineralogy and geochemistry, their ages and isotopic compositions broadly overlap. Zircons crystallized in various intrusions display LA-ICP-MS U-Pb ages ranging from ca.43.2 to ca.38.8 Ma, together with median initial εHf values ranging from +9.1 to +10.0. The latter indicates a dominant mantle-derived origin for these magmas. Complementary radiogenic isotope whole rock data will provide more details about the magmatic source of all these magmatic rocks. Such multi-disciplinary approach aims at understanding the genetic link between the different magmatic pulses of various composition. The question remains whether this geological setting results from various magmatic source processes, crustal differentiation processes or a combination of both?

From an ore deposit point of view, magmatic rocks of the Tejsar area host a low sulfidation epithermal Au deposit dated at ca. 41.5 Ma. The presence of the deposit highlights the existence of a hydrothermal system at Tejsar, which is also evidenced by different features affecting the nepheline syenite. However, the temporal relationship between the magmatism and the hydrothermal event remains unconstrained and therefore the genetic link is unclear. In addition, a younger magmatic pulse, dated at 28.4 Ma by zircon U-Pb, is also recognized in the area and characterized by a high-K calc-alkaline adakitic-like composition. The granite intrusion is crosscut by quartz veins hosting molybdenite mineralization. Despite a 10 m.y.-long gap in the magmatic history, this younger intrusion is also characterized by a mantle-derived origin with a median εHf of +9.4.

Further south in the South Armenian Block, the Amulsar, Bargushat and Meghri-Ordubad regions are three other study areas hosting Cenozoic mantle-derived magmatism associated with epithermal Au and porphyry Cu-Mo deposits (Moritz et al. 2016; Rezeau et al., 2016). All together, combined with our recent results on the Tejsar magmatic complex will certainly provide new insights into the understanding of the regional geodynamic evolution of the Lesser Caucasus and associated petrological processes leading to fertile magmatism. Moreover, the Tejsar area is located at the transition between the Turkish Eastern Pontides and the Lesser Caucasus, and therefore it represents a key location to understand the broad regional geodynamic context shaping the central part of the Tethyan orogenic and metallogenic belt.
Figure 1. Geological map of the Tejsar magmatic complex located on the northern part of the South Armenian Block (SAB). The SAB is the southern structural unit of the Lesser Caucasus. Maps modified after Bagdasaryan et al., 1969 and Moritz et al., 2016.

REFERENCES
Pyroxene geochemical evolution in a distal Pb-Zn skarn body, Madan, Bulgaria

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The metallogeny of the Madan ore field has been associated with the onset of early Oligocene extension-related magmatism in the Central Rhodopes of southern Bulgaria (Marchev et al., 2005). Pb-Zn distal skarn deposits were formed between 29.95-31.22 Ma (Kaiser-Rohrmeier et al., 2013, Hantsche et al., 2017], but little is known about the chemical evolution of the skarn system.

The prograde mineral assemblage in these skarns is dominated by Mn-rich pyroxene, which form spheroidal aggregates, replacing carbonate lenses within the metamorphic basement rocks. At the Petrovitsa deposit near Madan, the relationship between a skarn body and a mineralized vein has been characterized to study the geochemical evolution of a distal skarn system. Sections of preserved prograde skarn were sampled for petrography, bulk rock chemical analysis, and pyroxene geochemistry to better understand chemical evolution that occurs during formation of distal skarn systems.

Concentric growth bands in the pyroxene aggregates are observed at the hand sample and microscopic scale, and occur as variations in grain size and chemistry. Geochemical data from Electron Probe Micro Analysis (EPMA) and X-Ray Fluorescence (XRF) are presented to show variations in major element silicate geochemistry both at the thin-section and outcrop scale away from the vein. Pyroxene compositions, measured by EPMA, indicate hedenbergite [CaFeSi₂O₆]-johansennite [CaMnSi₂O₆] solid solution. Preliminary results show that alternating chemical compositions cycle between Fe-rich pyroxenes, which are typically fine grained (~1mm), and coarser, Mn-rich pyroxenes (~0.5 to 5 cm) (Figure 1).

Calcium data from the EPMA has been used as an internal standard for LA-ICP-MS trace element analysis. At the outcrop scale, whole rock geochemistry shows general decrease in Fe, Mg, Sr concentration away from the vein, with increase in Mn, Al, and Na compositions. Ongoing trace elemental analyses of pyroxene will be presented here for the first time.

Figure 1. Mn – Fe- Mg Elemental map from JEOL 8200 Superprobe at the University of Geneva.

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A geochemical and petrological study to constrain the magmatic history of St Kitts and Nevis (Lesser Antilles)

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Volcanic activity of St Kitts (Northern Lesser Antilles Volcanic Arc) is represented by a sequence of small volume volcanic domes and lava flows erupted over a timescale of 2 million years. The activity of the island is closed by explosive activity (1.8 kA; Harkness et al., 1994). St Kitts is a case study of a system that is active over a long period of time whilst erupting relatively limited amounts of magma. We intend to analyse samples spanning the entire eruptive history of the island to constrain the temporal evolution of magma geochemistry and the rate of magma supply in the plumbing system. These data will allow us to estimate extrusive intrusive ratios and characterise the processes responsible for the transition from mainly effusive to explosive activity.

We will present preliminary petrographic analysis of the rocks of St Kitts island as well as whole rock geochemical and trace element data. Preliminary zircon trace element data and U/Th model ages may be available, with the aim of using the statistical analysis of zircon age populations to constrain the magma flux (Caricchi et al., 2014). Cluster analysis of chemical zoning in minerals will be applied to obtain constraints on the chemical and physical architecture of the magmatic system over time. The same approach will also be applied to samples of St Martin and Nevis islands (Lesser Antilles).

This project is part of a wider study focusing on our understanding of the physical processes controlling the distribution of frequency and magnitude of volcanic eruptions we observe at a regional and global scale.

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P 2.16
Tectonic setting of the Cenozoic Kadjaran porphyry Cu-Mo – epithermal system, Armenia, Lesser Caucasus

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Recent structural investigations of the major porphyry Cu-Mo and epithermal systems of the southernmost Lesser Caucasus emphasize the fundamental role of regional strike-slip tectonics controlling these deposits and the associated magmatism during the Cenozoic geodynamic evolution of the Central Tethyan belt (Hovakimyan et al., submitted). In this study, we develop a tectonic model for the Oligo-Miocene evolution of the giant Kadjaran porphyry Cu-Mo system in southern Armenia. It is based on detailed district and deposit-scale structural mapping of the orientation and crosscutting relationships of dikes and mineralized veins, including kinematics along the major structures.

Paleostress reconstructions indicate three main tectonic events in the Kadjaran mining district (Fig.1). They are consistent with progressive anticlockwise rotation of paleostress orientations from the middle - late Oligocene to early Miocene, which was linked to the re-organization of the tectonic plates during Arabia-Eurasia collision. NNE-oriented compression and WNW-oriented extension during the middle to late Oligocene resulted in the activation of NS- and NE-oriented structures under dextral strike-slip tectonics. This regime is compatible with the emplacement of N- to NE-oriented early dikes reported by Tayan et al. (2002). The geometry and dominant NE- and NS-orientation of porphyry veinlets and veins dated from 27.3 to 26.4 Ma (Moritz et al., 2016; Rezeau et al., 2016) indicate that porphyry ore formation at Kadjaran occurred under a dextral strike-slip tectonic regime along NS- and NE-oriented structures. It is consistent with paleostress orientations reconstructed for the late Oligocene. During the late Oligocene, principal stress axes record a NS-oriented compression and EW-oriented extension, which reactivated ~NS-oriented structures and controlled the emplacement of fine-grained porphyritic granodioritic and lamprophyre dikes dated between 26.6 and 24.5 Ma (Rezeau et al. 2016), and crosscutting early NE-oriented dikes. During the early Miocene event, WNW-oriented compression and NNE-oriented extension resulted in reactivation of pre-existing structures in a sinistral strike-slip tectonic regime. This setting controlled the emplacement of ~EW-oriented coarse-grained porphyritic granogioritic dikes ranging from 22.2 to 21.2 Ma (Rezeau et al., 2016), which crosscut older dike generations and represent the youngest dike generation in the district (Tayan et al., 2002). An epithermal overprint affected the ore deposit during this event between 20.5 Ma and <22.2 Ma (Molybdenite Re-Os dating; Rezeau et al., 2016). Epithermal veins were mainly emplaced along ~EW-oriented fractures zones, but also along reactivated NS-oriented structures.
Figure 1. Tectonic evolution of the Kadjaran mining district and formation of the giant porphyry-epithermal system. Ages for magmatism and mineralization are from Moritz et al. (2016) and Rezeau et al. (2016). Dikes are based on a map by Tayan et al. (2002).

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P 2.17
Prograde metamorphism in the Bergell contact Aureole: A field and experimental study

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The Bergell intrusion, located between Switzerland and Italy, consists of a tonalite and a granodiorite body, which intruded at 32 Ma and 30 Ma respectively. In the upper Val Sissone, a several 100 m thick hornblende-gabbro has been newly found. The intrusion produced a well known contact aureole best studied in the eastern part of the intrusion, in the previously regionally metamorphosed serpentinites that underwent greenschist facies metamorphism (Trommsdorff and Connolly, 1996). With increasing metamorphic conditions, a sequence of reactions can be observed in Val Sissone that can be modelled in the CaO-MgO-Al2O3-SiO2-H2O (CMASH) system, representing lherzolitic protoliths (Stucki and Trommsdorff, 2001). At 400°C, 3 kbar reaction (1) antigorite + brucite = olivine + chlorite + water and the stable assemblage antigorite + olivine + chlorite + water + diopside is expected between 400 - 480 °C, representing regional greenschist facies conditions. Roughly 1.5 km from the contact reaction (2) antigorite + diopside = tremolite + chlorite + olivine + water produces the assemblage antigorite + olivine + chlorite + tremolite + water, stable between 480 - 520 °C. 750 m from the contact reaction (3) antigorite = olivine + talc + chlorite + water leads to the assemblage olivine + talc + chlorite + tremolite + water that is stable between 520 - 600 °C. 300 m from the contact Reaction (4) olivine + talc = anthophyllite + water forms the assemblage olivine + anthophyllite + chlorite + tremolite + water for an expected temperature range of 600 - 700 °C. This assemblage was previously identified to represent peak metamorphic conditions. However, at 100 m from the contact the reaction (5) olivine + anthophyllite = enstatite + water, with the assemblage olivine + enstatite + chlorite + tremolite/ hornblende + water is stable corresponding to temperatures of 700 - 730 °C. Moreover, in the first 40 m from the contact reaction (6) chlorite = olivine + spinel + enstatite + water and the assemblage olivine + spinel + enstatite + tremolite/ hornblende + water is stable, with a stability field extending between 730 - 820 °C. Reaction (7) olivine + tremolite = enstatite + diopside is not observed in the contact aureole. Furthermore, assemblage 5 shows inclusions of anthophyllite, olivine, chlorite and spinel in newly formed enstatite implying the coincidence of the two univariant curves anthophyllite-out and chlorite-out. Our study shows that in Val Sissone the contact metamorphic temperatures were underestimated by 150 - 200 °C at the contact of the intrusion to the serpentinite. While the general sequence of reactions can be well modelled in the simple system, many field observations such as the occurrence of hornblende, the transition from Cr- to Al-spinel and the width of the anthophyllite field are inconsistent with existing experiments in simple systems that do not contain Fe, Cr, and Na.

To fill this gap we also performed new experiments using natural serpentinitite powders that constitute the system FMCrASH (harzburgite) and NCFMCrASH (lherzolites) in cold seal experiments at 2 kbar from 625 to 725°C. From 625 - 675 °C, olivine, talc, chlorite, magnetite is the stable assemblage in the FMCrASH and additionally tremolite in the NCFMCrASH. At 700 °C olivine, talc, chlorite, Al-spinel and enstatite are stable in the FMCrASH as well as tremolite in the NCFMCrASH. Furthermore, at 725 °C olivine, enstatite, cordierite and Al-spinel occur in the FMCrASH and additionally hornblende in the NCFMcrASH. The hornblende-in reaction is observed at the chlorite-out reaction 5 indicating a continuous reaction between chlorite and tremolite increasing the tschermak and edenite component in the amphibole with temperature. Hence a new stability field consisting of olivine, enstatite, spinel and hornblende is proposed.

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High temperature crystal-melt reactions in mafic igneous complexes

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Magma chambers are built up incrementally, by repeated injections of hot melt, intruding as sills and dykes into pre-existing crystal mush and cumulate. Magma intrusion is not instantaneous but is a continuous flux over weeks, months or more. The total volume of intruded magma is difficult to estimate, as intrusive contacts are blurred by local reequilibration and segregation of interstitial melt and magma is drained back into the source after emplacement. In consequence, important heat input is neglected in our present perception of magma chamber dynamic. At high recharge rate or long-term magma flux (e.g. fast-spreading ridges, LIPs, arcs), high temperature crystals react with compositionally and thermally distinct intrusive melts (e.g. Leuthold et al., 2014, 2018). Here, I quantify the effect of gabbro cumulate melting and assimilation using 1-atm gas-mixing experimental petrology and compare with natural observations of ‘dry’ oceanic gabbro.

In gabbro protolith melting experiments (Tsolidus = 1140°C), hydrated cracked olivine and interstitial pigeonite melt to a dacitic liquid (F<0.01; 1150-1165°C) (Figure 1). The liquid changes to andesitic (F<0.02; 1180°C) and basaltic (F = 0.2; 1200°C) composition with increasing melt fraction and dissolution of clinopyroxene and plagioclase.

In hybrid picrite-gabbro equilibrium experiments, the clinopyroxene and plagioclase stability and the crystallization rate are increased (Leuthold et al., 2015). Cr-spinel abundance in picrite, gabbro and hybrid experiments is <0.5 vol%, unless under oxidizing conditions (≥NNO). The glass SiO2 and Mg# are increased, the olivine Mg# is increased and the clinopyroxene Mg# is increased and Al-content is decreased. The clinopyroxene REE concentration is decreased, despite a lower DREE.

In picrite-gabbro kinetic experiments reacted for 60 min at conditions where olivine, plagioclase and clinopyroxene are stable in gabbro but only olivine is stable in high-MgO basalt melt (1210°C, NNO-2), gabbro olivine and clinopyroxene are anhedral and plagioclase is euhedral. In the reaction rim, clinopyroxene is absent, olivine anhedral grains are small and Cr-spinel abundance strongly increased (to 1.8 vol%). With extended reaction duration, the reaction rim thickness is increased. Gabbro clinopyroxene grains are overgrown by high Mg# and Cr-rich rim, except in the direct proximity of spinel-rich layer.

As consequences:
1) High Mg# clinopyroxene in spreading ridges are frequently interpreted as crystals crystallized at high pressure or from primitive melt, but may alternatively result from mafic rock assimilation. Rocks microtextural and geochemical observations help to discriminate between processes.
2) Plagioclase reaction is frequently incomplete during partial melting, preventing achievement of global equilibrium, as previously demonstrated by Wolff et al. (2013) in hydrous oceanic gabbro experiments. I thus question whether troctolite cumulate and anorthosite result from gabbro partial melting.
3) Ore-bearing chromitite may crystallize from a hybrid melt, produced by gabbro assimilation by hot high-MgO basalt.
4) The partial melt and hybrid melt chemistry is distinct from the one produced by simple crystallization along the liquid line of descent of a mantle-derived melt. Reaction products are distinct from ‘defractionation’ process.
Figure 1. Gabbro partial melting (1-atm, NNO-2, 1165°C, 5h). Destabilization of interstitial Opx along grain boundaries and of hydrated cracked Ol. Generation of a dacitic melt (<1vol%). Eutectic Cpx and Plg are stable.

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P 2.19
Sodic amphibole and sodic clinopyroxene in the Dent Blanche (Western Alps): new constraints for an old question

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Determining the P-T conditions of Alpine metamorphism in the Dent Blanche Tectonic System (DBTS) is a difficult task because sensitive bulk-rock compositions are rare (hence the diagnostic mineral assemblages are lacking), and chemical equilibrium has rarely been achieved. Alpine greenschist facies metamorphism is dominant. However, few occurrences of sodic amphibole and sodic clinopyroxene may indicate early, blueschist-facies, metamorphism (first mention Stutz, 1940).

We report new field and laboratory results to better document the inferred high pressure history of the Dent Blanche.

Despite systematic search, we have been unable to find blue amphibole in mafic rocks (e.g. in the Permian metagabbros or in the pre-Alpine amphibolites). However, sodic amphibole and sodic clinopyroxene are found in different lithologies from several tectonic units of the DBTS (Mont Gelé and Regondi Units of the Arolla Series; Lower Unit of the Mont Mary). Field, petrographic and geochemical data indicate that these minerals form in different rock types, some approaching isochemical systems, the other requiring significant metasomatism. Three main occurrences have been found.

(i) Sodic amphibole forms coronas around magmatic calcic amphibole in undeformed pods of ultramafic cumulates (hornblendites).

(ii) In metasomatized granitic orthogneiss and leucotonalite, sodic amphibole mainly defines rosettes or sheaves, generally without a shape preferred orientation. Only locally they form needles aligned parallel to a mylonitic foliation and a stretching lineation. Pale green, patchy zoned aegirine augite is dispersed in an albite-quartz matrix or forms layers of fine-grained fibrous aggregates. Blue amphibole is slightly zoned with a darker blue core (mostly magnesioriebeckite) and a lighter blue rim (winchite).

(iii) In the Lower Unit of the Mont Mary, sodic amphibole and muscovite define an earlier foliation in fine-grained gneiss and are partially re-oriented parallel to a second schistosity. In these rocks, blue amphiboles display magnesioriebeckite cores surrounded by glaucophane rims.

Bulk rock chemistry of the different lithologies indicates a high Fe³⁺/Fe₄O₉ ratio (0.45-0.82). Thermodynamic modelling performed for different rock types (taking into account the measured Fe₂O₃ content) reveals that magnesioriebeckite and aegirine-augite are stable at 6-8 kbar and 400-450 °C.

In addition, preliminary geochronological results on the age of the Alpine metamorphism in the blue amphibole-bearing rocks will be presented.

These data provide better constraints on the Alpine metamorphic evolution of the DBTS, highlight the role of the Fe₂O₃ on stabilizing sodic amphibole and sodic clinopyroxene, and suggest significantly lower pressures for the DBTS than proposed previously.

REFERENCES
Polybaric fractional crystallisation of arc magmas - an experimental study

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Despite a still ongoing debate, differentiation of primary calc-alkaline liquids by fractional crystallisation is now generally accepted as one of the main driving mechanism controlling the compositional evolution of arc magmas. However, previous experimental studies failed to reproduce the predominantly metaluminous natural rock record by lower crustal crystal fractionation. At high pressures, experimental liquids rather evolve towards peraluminous compositions. The absence of abundant cumulates in the upper crust does not support the alternative scenario of major differentiation at low pressure conditions. Therefore, we propose an alternative process, namely polybaric fractional crystallisation, inferring that arc magmas differentiate progressively by crystal fractionation upon ascent through the crust. This hypothesis is tested through a series of experiments along several P-T ascent trajectories with continuously decreasing temperatures and pressures. Phase equilibria data, chemical compositions of stable mineral phases, liquid lines of descent as well as the evolution of crystal/melt ratios will provide crucial information to improve our understanding of the evolution of the calc-alkaline magmatic series and clarify if fractional crystallisation can be considered as a major process in the differentiation of mantle derived magmas at convergent plate boundaries. Our first experimental results support theoretical considerations on the effect of decreasing crystallisation pressure on mineral phase equilibria: the olivine-clinopyroxene cotectic curve is shifted towards more Cpx-rich compositions (equivalent to a destabilisation of clinopyroxene) rendering residual melts more metaluminous and, therefore, circumventing a rapid evolution of liquid lines of descent towards and into the peraluminous compositional field.
**P 2.21**

**Cenozoic magmatism in northwestern of Central Iran Block: Roll back, mantle upwelling and extension**

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The cenozoic Uromieh-Dokhtar Magmatic Arc (UDMA) of Central Iranian block comprises magmatic rocks, which are generally regarded as having been derived from the southern active margin of Eurasian plate (Fig. 1). The successions of lavas, pyroclastic deposits and intrusions of various thickness are elongated in NW-SE direction which are exposed within the UDMA. This study presents zircon U-Pb data analyses of intrusive rocks associated with geochemical data from the UDMA, central Iran. Eocene magmatic activities initiated from Ardestan (51-53) and Kashan (50-52) to Saveh (37-40), these volcanic successions largely comprise calc-alkaline rocks occurring as lava flows, pyroclastic layers, intrusives, tuffs and ignimbrites.

Post-collisional magmatic activities were started in Burdigalian (18-20 Ma.) in the Aleh dome (e.g. Qom region) and Langian (15-18 Ma.) in Khastak crater (e.g. Salafchegan region) and continued to Quaternary flood basalt (e.g. Ahar region) or along the later eruption in the Sahand (4.2-6.5 Ma.) and Sabalan (0.38 Ma.) volcanoes (Table 1). Geochronology observation show that not only the UDMA magmatism most active and widespread during Eocene and Oligocene (25-52 Ma.), but also continued to Neogene and Quaternary in post-collision setting, where trans-tensional basin system were working due to mantle diapirism and subduction rollback process. Such magmatism may generate from the convectively upwelling asthenosphere and/or thermally activated lithospheric mantle during local extension. These geochronological data together with geochemical data suggest that the late Paleocene-Eocene to Neogene to Quaternary magmatic flare-up was most active event in central Iran Block.

<table>
<thead>
<tr>
<th>No.</th>
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<th>Age (Ma.)</th>
<th>References</th>
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<tr>
<td>1</td>
<td>Ardestan (East of Esfahan)/Granodiorite</td>
<td>51-53</td>
<td>Sarjoughian &amp; kananian, 2017</td>
</tr>
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<td>2</td>
<td>Kashan/ Monzodiorite</td>
<td>50-52</td>
<td>Honarmand et al., 2013</td>
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<td>3</td>
<td>Saveh/Granodiorite</td>
<td>37-40</td>
<td>Nouri Sandiani et al., 2018</td>
</tr>
<tr>
<td>4</td>
<td>Sahand/Ignimbrite</td>
<td>4.2-6.5</td>
<td>Chiu et al., 2017</td>
</tr>
<tr>
<td>5</td>
<td>Sabalan/Andesite</td>
<td>0.38</td>
<td>Lin et al., 2011</td>
</tr>
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<td>6</td>
<td>Salafchegan/Quartz-monzodiorite</td>
<td>15-18</td>
<td>Monsef, current study</td>
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<td>7</td>
<td>Qom/Granodiorite</td>
<td>18-20.3</td>
<td>Monsef, current study</td>
</tr>
</tbody>
</table>

Table 1: Zircon U-Pb data results from northwestern Uromieh-Dokhtar magmatic arc
REFERENCES:
Relation between mean stress, thermodynamic and lithostatic pressure

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Pressure is one of the most important parameters to be quantified in geological problems. However, in metamorphic systems the pressure is usually calculated with two different approaches. One pressure calculation is based on petrologic phase equilibria and this pressure is often termed thermodynamic pressure. The other calculation is based on continuum mechanics, which provides a mean stress that is commonly used to estimate the thermodynamic pressure. Both thermodynamic pressure calculations can be justified by the accuracy and applicability of the results. Here, we consider systems with low differential stress (<1 kbar) and no irreversible volumetric deformation, and refer to them as conventional systems. We investigate the relationship between mean stress and thermodynamic pressure. We discuss the meaning of thermodynamic pressure and its calculation for irreversible processes such as viscous deformation and heat conduction, which exhibit entropy production. Moreover, we demonstrate that the mean stress for incompressible viscous deformation is essentially equal to the mean stress for the corresponding viscous deformation with elastic compressibility, if the characteristic time of deformation is 5 times longer than the Maxwell viscoelastic relaxation time that is equal to the ratio of shear viscosity to bulk modulus. For typical lithospheric rocks this Maxwell time is smaller than approximately ten thousand years. Therefore, numerical simulations of long-term (>10 kyrs) geodynamic processes, employing incompressible deformation, provide mean stress values that are close to the mean stress value associated with elastic compressibility. Finally, we show that for conventional systems the mean stress is essentially equal to the thermodynamic pressure. However, mean stress and, hence, thermodynamic pressure can be significantly different from the lithostatic pressure.
Most of the calc-alkaline and alkaline magmatic rocks in the South Apuseni Mountains were emplaced between 7.4 and 14.7 Ma (based on K-Ar dating) along NW-SE oriented graben structures, and as clusters of magmatic bodies (Rosu et al., 2004). Even though some of the magmas show an adakite-like character typical for subduction zones, they are the result of decompression melting of a previously metasomatized mantle, followed by asthenosphere upwelling. The reason for this decompression and the easier ascent of the magma through the continental crust is thought to be the consequence of rotational tectonics that created pathways with the horst and graben structures (Rosu et al., 2004; Neubauer et al., 2005; Harris et al., 2013).

Associated with this Miocene magmatism are several Cu-Au porphyry and epithermal deposits, which gave the region the name ‘Golden Quadrilateral’. Euro Sun Mining Inc. has the license for exploration and mining of four of these porphyry deposits, which are situated in the Rovina Valley Project and Stanija Prospect, respectively. To better understand the relationship between the different intrusions and their mineralization potential we performed U-Pb age dating on zircons by LA-ICP-MS and ID-TIMS on several drill core and outcrop samples. Furthermore trace element compositions, rare earth elements and Hf isotopes were analyzed to characterize differences in the magma composition and thereby unravel heterogeneities in the magma source region.

First results show that three of the sampled deposits are similar in age (around 12.4 Ma), and formed at a time that was very favorable for the formation of porphyry deposits in terms of the tectonic regime as well as the generation of fertile magmas. The fourth deposit is significantly younger (around 11.3 Ma) and is connected to a later magmatic phase that was different in terms of magma evolution. Heterogeneity between the magma source regions is also visible in the Hf isotope ratios. The results of ID-TIMS point out that the youngest porphyry deposit was formed within a very short time span of only a few 10'000 years, what is consistent with recent results on Cu porphyry deposits (Buret et al., 2016).

REFERENCES
P 2.24

Carbonate clumped isotope climate reconstructions on fossil coral samples of the Early Eocene

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The climate of the Early Eocene is often referred to as a potential climate analog we are currently heading to. The atmosphere during the Early Eocene contained extremely elevated concentrations of the greenhouse gas CO₂ and published studies on this period found no evidence of Polar ice caps. The lack of Polar ice caps and the elevated pCO₂ lead to a much warmer climate conditions that were completely different to our modern time.

Climate reconstructions from localities close to the Polar circle revealed temperatures between 20 to 30 °C and tropical flora/fauna was widely found in this area. In general most of this data revealed smaller meridional temperature gradient between the Equatorial and Polar regions, which current climate models struggle to reproduce.

In our study we applied carbonate clumped isotope thermometry on fossil coral samples recovered from the Southern coast of Australia, which had an Early Eocene latitude of more than 60 ° South. Our Early Eocene climate reconstructions on the fossil corals that probably grow in the mixed layer close to the surface offer new temperature data from this period that are probably more annual temperatures and thus are a bit colder than other published climate proxies in this area.
A geochronological study of zircon and zirconolite observed in ruby and spinel gemstones and in marble host rock from Mogok, Myanmar

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The Mogok area within the Mogok Metamorphic Belt (MMB) in Myanmar is famous worldwide for its high quality ruby and spinel deposits. Although MMB has been studied extensively in terms of petrography, geochronology and tectonics, only very limited data so far have been reported on U-Pb ages of zircon specifically from the Mogok area, which is a significant segment of the MMB. Our research focuses on U-Pb age dating of zircon and zirconolite inclusions from gem-quality ruby and spinel as well as from marble host rock from the Mogok area to better understand the complex metamorphic events leading to their formation.

Samples were collected in the Mogok area during a field trip in 2016. In the course of gemmological and petrologic studies, zircon inclusions were identified and imaged by Raman spectrometry and scanning electron microscopy. Zoning in zircon was observed using CL-images of a scanning electron microscope equipped with a variable pressure secondary electron detector (VPSE). Zircon and zirconolite inclusions in gemstones and marbles were analysed with LA-ICP-Time-Of-Flight (TOF)-MS and LA-ICP-Sector-Field (SF)-MS using a crater size of 35 µm in TOF-MS and a crater size of 20 µm and 13 µm for SF-MS on small grains and strongly zoned grains. The age dating results by these two methods are well in accordance with each other. Besides geochronology, trace element composition of zircon and zirconolite were analyzed with TOF-MS, which can measure the full mass spectrum from Li to U simultaneously.

The zircon inclusions from gem-quality ruby and spinel mostly show distinct circular zoning in the core, with thick to thin-zoned rims. Some zircons in ruby from Mansin (Eastern Mogok) contain aggregated zircon grains with irregular overgrowth structures at their rims (Fig. 1a). Zirconolites from gem quality ruby are present as subhedral grains whereas zirconolites in marble host rock occur as inclusions within zircons or as rims of zircon (Fig. 1b). They are homogeneous and without zoning in CL-images.

The U-Pb ages of zircon inclusions in gem-quality ruby and spinel revealed two age groups: (1) late Cretaceous (~75 Ma), and (2) late Oligocene (~25 Ma). Zircons from ruby- and spinel-bearing marble from Bawlongyi (western Mogok) yielded a wide range of similar ages 75-25 Ma. In addition, zirconolites from gemstones and ruby- and spinel-bearing marbles yielded ~21 Ma. Our results are well in accordance with Cretaceous to Miocene ages of intrusive igneous rocks, i.e. diorite, granite and granite dykes by Andrew Mitchell et al (2012). The wide range of U-Pb ages indicates several metamorphic events that took place in the Mogok area with the latest event in Early Miocene. Our investigations show that the formation of gem-quality ruby and spinel in the Mogok area most probably took place during the latest metamorphic event.
REFERENCES
High precision Ar/Ar age traverses reveal intragrain inhomogeneities of pristine magmatic micas

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Micas are among widely used minerals for interpretation of the age and duration of magmatic and metamorphic processes. Such interpretations are based on the assumptions that micas were either closed since crystallization/re-equilibration, in which case they yield a flat step-heating age spectrum, or underwent a partial re-opening of the system that is reflected by a discordant age spectrum.

To assess the validity of such assumptions we studied two pristine-looking magmatic museum-grade mica megacrysts, whose Rb-Sr age coincides with the U-Pb age of co-existing minerals.

The first sample, consisting of five phlogopite sheets, 0.2-0.8 cm large, comes from the Phalaborwa carbonatite (NE Transvaal, South Africa), layered intracratonic alkali complex composed mainly of clinopyroxenites with minor carbonatites and phoscorites that intruded an Archean terrain (Eriksson, 1984). All layers of the intrusion have been dated by U-Pb (baddeleyite, zircon) at 2060 ± 3 Ma (Wu et al., 2011), the phlogopite used for this study has been previously dated with Rb-Sr method at 2059 ± 5 Ma (Naumenko-Dèzes et al., 2018).

The second sample, consisting of two 0.8-1.0 cm large muscovite sheets, comes from the Rubikon pegmatite body (Namibia) dated with U-Pb at 505Ma (Melcher et al., 2015). Each grain was cut with a metal blade to create age profiles, each individual piece (ca. 100x1000µm in size) of such profiles was separately irradiated and measured either with an ArgusVI (Nice) and/or a Noblesse (Milano) multicollector mass-spectrometer, step heating by laser (Nice), respectively furnace (Milano).

In all cases we obtained a plateau. Despite this apparent proof of ideality, each piece has a different age (up to 5 %) from its neighbors, without any core-rim relationship (Fig 1a). Such age inhomogeneity also corresponds to compositional inhomogeneity that can be traced for some samples by Ca/K vs age positive correlation. Indeed, quantitate microprobe data for Phalaborwa phlogopite showed alteration bands (3-30µm) along cleavage planes that are marked by a decrease of Ti, Fe, Al and an increase of Mg and Si. Quantitative microprobe data for Rubikon muscovite showed compositional changes (Al, K and Mn) parallel to cleavage planes as well as zones of different composition perpendicular to the cleavage planes (Fig.1b). Patchy intra-grain zonations are diagnostic of altered minerals (Villa & Hanchar, 2017) and support the interpretation that late post-magmatic fluid circulation disturbed both the magmatic chemical zonation and the K-Ar system. In summary, we observe that even museum-grade magmatic micas may show a patchy disturbance of both the K-Ar system and major element composition.

Fig. 1. (a) Ar/Ar age variation within a muscovite grain; (b) Al₂O₃ variation in a muscovite sample, perpendicular to the cleavage mount.
Variations in Ti, Mg and Al concentrations for phlogopites as well as Mn, K and Al for muscovites correspond to more than 5% Ar/Ar age variations inbetween subgrains, even though each individual subgrain gives an “age plateau”. The data of this detailed case-study require that correlated intra-grain compositional and age variations be ascribed to hydrothermal events postdating the major phase of magmatic crystallization, and not to a simple temperature-driven diffusion history.

REFERENCES
Spinel Iherzolite xenoliths from the Cameroon Volcanic Line (CVL): Implications for mantle processes and equilibrium conditions

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Spinel-bearing xenoliths recovered from Cenozoic alkaline basalt flows of the Wum volcano, located in the central part of the Cameroon Volcanic Line (CVL), at N°6°24' and E10°04' have been examined to characterise the petrography, mineral major and trace element composition, water contents and conditions of equilibration of the mantle below the region. Investigated xenoliths are spinel Iherzolites showing well equilibrated protogranular textures. One Wum sample contains amphibole, which has not been previously reported in this locality. Two-pyroxene thermometry based on major element exchange yields temperatures of about 930 ± 110 °C assuming a pressure of 15 Kbar, consistent with the spinel stability field. Temperatures estimated from Ca (980 °C), Al (955 °C) and Cr (995°C) thermometers in olivine show a good correlation between the three methods but are higher than the two-pyroxene thermometers. Calculated temperatures based on REE partitioning between clinopyroxene and orthopyroxene are around 1050 °C and are generally higher than the temperatures determined from trace elements in olivine. The water contents of olivines and pyroxenes were determined by FTIR spectroscopy using unpolarised light on unoriented crystals. Olivine typically contains <1 ppm H₂O, whereas orthopyroxene and clinopyroxene have water contents of 17-35 ppm and 85-170 ppm at their cores respectively. Calculated inter-mineral partition coefficients indicate that H distribution is not at equilibrium, typical for mantle samples which have experienced diffusive water loss during ascent, supported by a decrease in water content from core to rim in orthopyroxene. Patterns of rare earth element normalised to primitive mantle values (Palme and O’Neill,2013) of clinopyroxene show different groups: the first group with a depletion in LREE, the second with an enrichment in the LREE and a third group that shows no enrichment or depletion. These patterns reflect different stages of partial melting and metasomatism. Our new data indicate that the xenoliths came from a shallow part of the lithospheric mantle having imprints of several depletion and enrichment events. The high equilibration temperatures suggest extension in the lithospheric mantle related to heating prior to the entrapment of the xenoliths in the alkaline lavas. Moreover, the fact that clinopyroxene with different trace element patterns are present indicates that at least one metasomatic event must have occurred during this extension. Further work will exploit the relationships between melt production in the mantle, metasomatism and crustal evolution in the specific tectonic setting of the CVL.

REFERENCES
Convection of seawater through the hot oceanic crust has vast geochemical consequences: it modifies the composition of the crust via hydrothermal reactions, it forms valuable ore deposits, it buffers the composition of the oceans and, via subduction, it influences the composition of arc magmas and the mantle. Current knowledge of alteration in oceanic crust is strongly influenced by ocean drilling studies. However, ophiolites provide more representative insights into lateral variations in alteration. For example, the volcanic sequence of the Emeishan Ophiolite—the world’s largest sub-aerial exposure of oceanic crust—is pervasively altered. The basalts in recharge zones are converted to spilite (chlorite–albite–quartz) assemblages while in discharge zones they are transformed to epidosite (epidote–quartz) assemblages. Massive sulphide deposits, which are common in the ophiolite, are thought to be the final venting sites for these hydrothermal systems. In order to quantify the extent and impacts of the recharge alteration, we are characterising the geochemistry and mineralogy through a complete section of spilitised upper crust in the Emeishan ophiolite. We have sampled along transects from the sheeted dyke complex (SDC) to the top of the volcanic pile. The samples have been characterised by petrography and analysed by X-ray diffraction (XRD), X-ray fluorescence (XRF), carbon-nitrogen-sulphur (CNS) analysis, and ICP-MS. Our results confirm an increasing metamorphic grade with stratigraphic depth from brownstone facies (clay-dominated) to zeolite facies (zeolites, celadonite) to greenschist facies (chlorite, actinolite). This ‘peak’ grade, however, is partially overprinted by late low-temperature alteration. Unravelling this overprinted sequence by paragenetic arguments is key to knowing when particular mineral reactions took place during the maturation of this crust and has important implications for the availability of metals for VMS formation.
P 2.29
Unravelling magma emplacement mechanism in the lower crust: A forensic investigation of the Mafic Complex, Ivrea-Verbano Zone (Italy)

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The Ivrea-Verbano Zone (Southern Alps, Italy) is a unique target for assembling data on magma emplacement mechanism in the Earth’s lower crust. In its southern portion cross-cut by the Mastallone (north), Sesia (central), and Sessera river (south), the 13-km thick Permian Mafic Complex consists of hornblende-gabbro (lower part), gabbro-norite (intermediate part) and diorite (upper part), emplaced into a pre-Permian metasedimentary sequence, and represents the deep roots of the Permian Sesia Magmatic System. New field data (foliation and lineation measurements), three-dimensional analysis of oriented rock microstructures by X-ray tomography (50-μm spatial resolution), and calculations of physical properties (rock density, P- and S-wave velocity) based upon mineral chemistry and modal proportions indicate a magma body constructed by the repetitive emplacement of sills. We observe from bottom to top: a) a 2-km thick, cumulate region with an upward increase of pyroxene/amphibole (up to 75%) and oxide content (up to 6%); b) a 10-km main region preserving two 1- to 2-km thick pyroxenite intrusions interlayered with two 4-km thick plagioclase-dominated (up to 80%) zones in the body core, with its northern margin also characterised by presence of garnet (up to 77%); c) a 1.5-km portion composed of a hornblendite embedded in a biotite- (up to 20%) and plagioclase-dominated (up to 60%) region. Respective ~20% and 13% rock density and seismic velocity variations between plagioclase-rich regions and pyroxenite intrusions suggest an internal stratification of physically distinct portions. Indeed, P- to S-wave velocity ratios (V_p/V_s) show a body constructed by mafic pulses (V_p/V_s = 1.75-1.79), denser than the basal cumulate region, overlain by less dense regions (V_p/V_s = 1.84-1.87), which are able to intermingle with and assimilate metapelite septa of the pre-existing crust and, potentially, evolve into a K-rich hydrous body at the roof portion. The Mafic Complex architecture is therefore not the result of a catastrophic gravitational collapse of the pluton during crustal thinning, as previously proposed upon observation of upwardly concave layering and foliation in ophiolitic gabbros, but rather an incremental emplacement of pulses adapted to the geometry of the pre-existing crust.
P 2.30

U-Pb baddeleyite geochronology: two case studies from the western Avalon Peninsula, Newfoundland

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Baddeleyite ZrO2 is one of the most commonly used geochronometers for mafic rocks. Compared to zircon, baddeleyite is more robust to Pb loss, but small degrees of discordance are common and cannot be eliminated by chemical abrasion techniques. The mechanisms responsible for this discordance are not well understood, but crucial for accurate age interpretation. Aiming for an improved understanding of natural baddeleyite U-Pb systematics, we performed a case study on early Paleozoic dikes and sills of the Spread Eagle Intrusive Complex (SEIC) and Cape St. Mary’s sills (CSMS) of the Avalon Zone of Newfoundland (Canada). We combine detailed microtextural observations with U-Pb geochronology by secondary ionization mass spectrometry (SIMS) and thermal ionization mass spectrometry (TIMS).

Stratigraphically constrained intrusion ages are ca. 495-510 Ma (SEIC) and 400-500 Ma (CSMS). Low grade metamorphism took place during the Acadian Orogeny (ca. 360-420 Ma). Baddeleyite is often intergrown with zircon in four texturally different assemblages: (1) baddeleyite with younger metamorphic zircon rims, (2) baddeleyite with coeval igneous zircon, (3) baddeleyite with older xenocrystic zircon inclusions (one SEIC sample), and (4) altered igneous zircon with secondary baddeleyite inclusions (one CSMS sample). SIMS analysis (e.g., Schmitt et al. 2010) was performed either in thin section (in situ) or on crystal separates (grain mounts), to further distinguish and constrain the petrologic significance of these textural types. Selected crystals from grain mounts were subsequently used for single crystal TIMS analyses.

SIMS in situ results are, within error limits, concordant and in good agreement with the stratigraphic estimates, even in samples with baddeleyite crystal diameters <10 µm. However, some grain mount samples yielded reversely discordant data, resulting in overestimated 206Pb/238U ages, although this problem did not occur in secondary reference baddeleyite analyzed in the same sessions. TIMS data agree with SIMS in situ results and stratigraphic estimates, but are always normally discordant. Replicate TIMS analyses indicate variable discordance in SEIC baddeleyite, whereas CSMS baddeleyite analyses cluster at moderate discordance (Figure 1).

Reverse discordance in SIMS analyses is probably due to bias in the U/Pb relative sensitivity calibration. This could be due to beam overlap onto zircon intergrown with baddeleyite, but microtextural inspection suggests that other yet unidentified factors play a role. 206Pb/207Pb ages are insensitive to the calibration, but precision is often compromised by high common Pb. For SIMS analysis, surface contamination and/or contributions from adjacent phases are possible sources of common Pb. However, steady common Pb intensities even for some analyses with spots entirely on baddeleyite suggest that some common Pb is intrinsic to these crystals, as it is known from metamict zircon.

The complex pattern of SEIC analyses requires mixing between at least three age components, micropetrographically identified as: (1) magmatic baddeleyite crystallization, (2) metamorphic zircon formation, and (3) Pb loss in zircon. Ideally, baddeleyite and zircon domains should have been separated chemically prior to TIMS analysis using the step dissolution method of Rioux et al. (2010), but small crystal size of and/or radiation damage in zircon may have defied complete separation. The SEIC TIMS results allow only to broadly confine the intrusion age (>485 Ma), which is better approximated by the SIMS 207Pb/206Pb date (497 ± 7 Ma). Due to the spatial resolution of ca. 10 µm, intergrown zircon domains can be avoided more easily by SIMS. Secondary zircon domains are much more rare in CSMS baddeleyite than in SEIC, so another process must be responsible for the discordance observed in both methods. Previously hypothesized mechanisms for baddeleyite discordance (e.g., alpha recoil, radon loss, or protactinium excess) have different consequences for U-Pb systematics, resulting in permissible ages from 430.8 ± 0.4 Ma to at least 438.7 ± 2.4 Ma (2σ) for the CSMS sample. This study shows that baddeleyite geochronology can yield accurate ages in favorable circumstances, but also that U-Pb systematics for baddeleyite from mafic rocks affected by typical low-grade metamorphism are not simple. Further studies are necessary to identify the dominant processes responsible for baddeleyite discordance. To enhance baddeleyite geochronology, multi-method approaches with a focus on microtextures are useful.
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Epidosite formation in the oceanic crust: Composition and P–T properties of the metasomatizing fluid

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Epidosites are former igneous rocks (dikes, lavas, trondhjemite intrusions) that have been hydrothermally altered to epidote + quartz + titanite + Fe-oxides. They have been proposed as markers of deep upflow in sub-seafloor hydrothermal convection cells, and as sources of metals in seafloor black-smoker sulphide deposits. In order to test these proposals by geochemical modelling, the composition of the metasomatizing fluid and the P–T conditions of alteration must be identified.

Fluid inclusion studies have reported evidence from diabase dikes that epidosites formed from aqueous solutions with seawater salinity (e.g. Nehlig and Juteau, 1988). In apparent contradiction, other studies have provided fluid inclusion evidence from altered trondhjemites that epidotization was caused by hypersaline brines (e.g. Cowan & Cann, 1988; Juteau et al., 2000).

We have collected epidosites from the sites of the original studies in the Semail (Oman) and Troodos (Cyprus) ophiolites and reexamined their fluid inclusions. Our analyses of primary inclusions in epidote and coeval quartz confirm that epidotization of basaltic dikes and lavas was due to solutions with seawater salinity (~ 4.0 wt.% TDS). In the epidosites overprinting trondhjemites we also discovered primary aqueous inclusions with the same salinity, in contrast to the earlier studies. The primary hypersaline inclusions in these rocks, reported by previous workers, are confined to paragenetically earlier hydrothermal–magmatic quartz and hence they are unrelated to epidotization. Since these brines coexist with inclusions of water vapour, they represent phase separation of either magmatic water or early infiltrations of seawater.

Temperature and pressure reconstructions from the fluid inclusion data reveal that epidotization occurred over a range of conditions, from 240 to 440 °C at hydrostatic pressures of 25–50 MPa. Thus, both the P–T conditions and the Ca-enriched, Mg-depleted fluid composition are consistent with epidosites representing upflow zones of deeply convected seawater.

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Comparative study of XRF and portable XRF analysis and application in hydrothermal alteration geochemistry: The Elatsite porphyry Cu-Au-PGE deposit, Bulgaria

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X-ray fluorescence (XRF) spectrometry is a non-destructive analytical technique widely used in Earth and Environmental Sciences to determine the elemental composition of rocks, ores, soils and plants. Portable XRF analysers (pXRF) are increasingly being used in mineral exploration and mining, allowing acquiring rapidly and inexpensively large geochemical data sets in the field. In this contribution, we present the results of a comparative study of 15 samples of hydrothermally altered magmatic and metamorphic rocks from the Elatsite porphyry Cu-Au-PGE deposit in Bulgaria, using both a lab-based WD-XRF (PAnalytical AxiosmAX) and a pXRF (Thermo Niton XL3t) device.

For analyses performed with the pXRF, the samples were crushed to a fine-grained powder (<80 μm) and mounted in a plastic cup covered by a thin polypropylene film (4 μm-thick) to be analysed on a test stand. Two techniques for sample preparation were used, resulting in slight difference in compaction of the sample measured: the first one consists of analysis of non-pressed powder in the cup (referred to as “powder” in Fig. 1), and in the second case the powder is slightly compressed with an agate pestle (referred to as “pressed powder” in Fig.1). A total of 34 elements were measured using the “Soils & Minerals” protocol within the “Mining Cu/Zn” mode of the pXRF. Measurements were 120s each consisting of two 60s cycles using four different energy filters. For some elements (Al, V, Mn, Mo, Ba) pressed-powder samples show systematically slightly higher values (as high as 10%; Fig. 1C).

Lab-based WD-XRF results were used to perform an empirical calibration of the elemental concentrations obtained by pXRF, following the procedure proposed by Mauriohooho et al. (2016) (Fig. 1A-B). Linear regression analysis of the data allows calculating the correction factor to be applied (corresponding to the slope of the regression line) for each element determined by pXRF. For each filter, the correction factor decreases progressively with the increase of the atomic number of the measured element (Fig. 1D).

Comparing the results obtained using the two sample preparation techniques for the pXRF analyses, we demonstrate that generally both of them provide accurate data comparable with WD-XRF (Fig. 1B), resulting in correlation coefficients >0.9. However for some elements (ex. Al, Sr, Zn), pressed-powder preparation resulted in better correlation between WD-XRF and pXRF analyses.

Unfortunately, due to its low atomic number, Na cannot be quantified by pXRF, and Mg is usually measured with a low level of confidence.

Our results demonstrate that large data sets obtained with a pXRF device can be used after correction based on lab-XRF analyses on selected representative samples for geochemical interpretation on suites of hydrothermally altered samples (mass balance and alteration index calculations).
Figure 1. Comparison between lab-based WD-XRF and pXRF analyses of hydrothermally altered rock samples: A) K concentrations of powder and pressed-powder samples vs. lab-XRF analyses; calculated slopes from regression analysis are used as correction coefficients; B) Corrected values of K concentrations from pXRF analyses vs. lab-XRF data; C) Powder vs. pressed-powder sample preparation for pXRF analyses (Al concentrations); D) Correction factor as a function of Z (atomic number) of the elements for the four different filters used (light, low, main, high).

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P 2.33
How to achieve 100 ppm precision on a U-Pb zircon age: recent developments and their limitation

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U-Pb geochronology has seen unprecedented developments during the last few years. The run for higher and higher precision of dates from ever lower volumes of material (especially zircon) has required a series of innovations: chemical pre-conditioning of sample material, micro-sampling, highly precise and reproducible micro-chemical procedures, and innovations in low-level mass spectrometry. At the same time the needed volume of zircon for isotope-dilution TIMS dating became equivalent or dropped below that sampled by laser-ablation ICP-MS, but is still largely higher than that ablated by secondary ion beam mass spectrometry techniques. This talk will give an outline of the main developments that were necessary to achieve our presently best precision of 0.01-0.02% for an ID-TIMS 206Pb/238U age of a geological sample, from improvements in low-volume microchemistry, to mass spectrometry techniques.

Achieving long-term, intra-sample, and intra-laboratory reproducibility at the 0.01-0.02% level is by far more challenging than it is for precision. We will show data that document (i) our continuous efforts to assess accuracy; (ii) our tests of system reproducibility with natural reference materials or synthetic reference solutions; and (iii) our results of intercalibrating our two TIMS platforms (a 15 years old and recently upgraded Triton from Thermo Scientific vs. a recent Phoenix from IsotopX) at the same level of precision.

Examples how improved temporal resolution can offer new insights into fundamental questions of planetary dynamics comprise synchrony of large igneous provinces, dramatic change of the Carbon cycle and associated mass extinctions, the role of internal vs. external forcing in climate change, or the role of large-scale continental glaciations for major evolutionary discontinuities in the biosphere recorded in the geological past.
Soapstones: fields and production laboratories between Ticino and Moesano

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The soapstone fields known along the Alpine mountain range in the territory of France, Italy and Switzerland are about ~400 of which 120 are located in Southern Switzerland (Ticino and Moesano) together with 14 production laboratories. The extraction, the use and the function of soapstone manufactories have influenced the historical and economical evolution of Alpine ethnographic contexts since the Iron Age, with a peak of production of pots (“laveggi”) between the last centuries of the Roman Empire and the Late Middle Ages. From the XII century the soapstone was also used for stoves and in architecture as documented in the romanic S. Nicolao church in Giornico.

The recovery of this historical identity is based on the study of archeological artifacts and on the reconstruction of historical commercial networks. For this purpose, tracing back the extraction site of an archeological artifact becomes fundamental to reconstruct the ancient commercial roads across the Alps. The mineralogical content of soapstone artifacts has successfully been used to distinguish the provenance of artifacts coming from the Valtellina or from the Val d’Aosta. However, the petrographic method shows some limits because several types of soapstone can be found in more than one Alpine region. Here, we present (i) a database of soapstone fields and production laboratories updated after Pfeifer and Serneels (1986) and Mannoni et al. (1987) that includes new findings and (ii) new bulk-rock geochemical analyses to support the petrographic characterization of soapstones. The small differences in mineral and in major- and trace-elements compositions should help to localize the fields.

Eight types of soapstone can be distinguished in southern Switzerland; some of them are characteristic of a specific area. The preliminary geochemical results show that the chemical composition can be significantly different even between the same type of soapstone and that H₂O and CO₂ (LOI), U and Cr can be tentatively linked to the metamorphic grade and the mineralogy of the soapstone, permitting to better reconstruct the geological framework of the rock and therefore also the location from which it has been extracted.

Even though the geochemical implications need further analyses to be verified, this preliminary study shows that the geochemical characterization is an added value to the study of the archeological artifacts of soapstone.

Figure 1. Soapstone pots of Roman Period and of Modern Epoch, coming from archeological sites in Ticino (©Ufficio dei beni culturali, Bellinzona).
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On CF$_4$ – a trace gas in granites and in the past atmosphere

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In 1966, pioneering geochemical trace gas analyses of fluid inclusions revealed that natural fluorite contains significant amounts of polyfluorinated organic compounds (Kranz, 1966). It turned out much later that one of these compounds, tetrafluoromethane (CF$_4$), can be found as well in the preindustrial atmosphere at a concentration of around 36 ppt (parts per trillion), a mass of around half a million tonnes (Harnisch et al., 1996). Further analyses revealed that CF$_4$ is not only present in fluorite samples, but also in granites and gneisses (Harnisch et al., 2000). It is assumed that CF$_4$ is produced and enclosed in the accessory fluorite crystals that are present in some granites. Several pathways were suggested that involve e.g. F$_2$ produced at lattice defects within the CaF$_2$ crystal that reacts with CO$_2$ or organic carbon within the fluid inclusions to form CF$_4$. In addition to CF$_4$, a suite of other fluorinated compounds have been identified, like SF$_6$ and NF$_3$, suggesting that a reservoir of F$_2$ reacts with any impurities available in the CaF$_2$ crystal. The CF$_4$ content of granites shows a large spread that may reflect different mineralogical composition or cooling history.

The release of CF$_4$ into the atmosphere due to processes that allow CF$_4$ to escape from the fluid inclusions (e.g. weathering or tectonic processes) leads to a built-up of CF$_4$ in the atmosphere (Harnisch et al., 2000; Deeds et al., 2015). CF$_4$ is a chemically very stable gas and natural destruction processes are only possible above an altitude of around 50 km in the mesosphere and thermosphere. Therefore, already small emission fluxes in the range of several tonnes CF$_4$ per year are required to generate this natural CF$_4$ background. The observed atmospheric CF$_4$ concentration at any time in the past is therefore a function of the global emission flux (e.g. from weathering of granites) and the atmospheric sink flux. Experimental studies and chemical transport models estimate the lifetime of CF$_4$ to be around 100,000 years. This extreme lifetime results from the fact that the entire volume of the troposphere and stratosphere has to be transported into the mesosphere and above.

In this presentation we show our 800,000 year long record of atmospheric CF$_4$ using air trapped in Antarctic ice core samples. This record documents systematic changes of the past atmospheric CF$_4$ concentration that are related to major changes in global climate. The main feature of our CF$_4$ record are changes that parallel the glacial/interglacial cycles with pronounced and rapid CF$_4$ increases during the deglaciations at the end of each glacial cycle. We interpret these deglacial CF$_4$ rises as pulses from increased weathering of granitic source material. Warmer climate, increased rainfall and runoff generally favour chemical weathering rates, thus are consistent with CF$_4$ rises during the deglacial phases. Additionally, the large North American and Fennoscandian ice sheets generated large amounts of moraine material that was transported towards the southern edges of these ice sheets. With the disintegration of the large ice sheets during the deglaciation, vast previously glaciated areas and forelands were left behind covered with fresh material. As fluorite is rather soluble in water, CF$_4$ could be released from the granites already at an early weathering phase at the start of the interglacial.

The second feature of our record is a long-term increase of CF$_4$ starting at around 420 kyr that is superimposed on the glacial/interglacial cyclicity. The onset of this long-term rise occurs at a distinct point in time as this period marks the Mid-Brunhes event (MB). Interglacial warm phases occurring after the Mid-Brunhes event are typically more intense (e.g. higher glacial/interglacial cyclicity. The onset of this long-term rise occurs at a distinct point in time as this period marks the Mid-Brunhes event (MB). Interglacial warm phases occurring after the Mid-Brunhes event are typically more intense.
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P 2.36

A method for determining magmatic volatile records by FTIR analysis of unexposed melt inclusions and their minerals hosts

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Melt inclusions provide one of the few opportunities to directly measure magmatic volatile concentrations. Transmission Fourier transform infrared spectroscopy (FTIR) is an accurate, precise and cost-effective method of achieving this. However, sample preparation is highly challenging, requiring that crystals are individually polished such that melt inclusions are double-exposed at both top and bottom surfaces and then their thickness precisely determined. This is not only time-consuming and difficult, but results in the destruction of almost the entire crystal and the remaining volatile record contained within. Here we show that the attenuation of the infrared absorption band relating to the Si-O structure of the quartz at 2136 cm⁻¹ can be used to determine the thickness of melt inclusions in quartz crystals several hundred microns thick without the need to double-expose. This thickness estimate can then be used in combination with O-H related absorption at 5230 cm⁻¹, 4520 cm⁻¹ and C-O related absorption at 2350 cm⁻¹ to calculate water concentration, water speciation and CO₂ concentration. Principle advantages of this method are much quicker and easier sample preparation, the ability to measure many melt inclusions per crystal and to assess variations of volatile contents in inclusions trapped in the core and the rim of the host. Additionally there is the possibility to combine this with complementary measurements of OH within the host mineral itself to assess volatile equilibrium.

We demonstrate the effectiveness of this method by reporting H₂O and CO₂ for 38 melt inclusions trapped within 11 quartz crystals from the 1.3 Ma Mesa Falls Tuff, Yellowstone Volcanic Field. H₂O and CO₂ concentrations average 3.1± 0.3 wt.% and 129 ± 46 ppm respectively, with CO₂ showing a much greater spread in concentration over relatively invariant H₂O. In general there are no significant differences between volatile concentrations of fully encapsulated melt inclusions at the crystal cores and rims indicating limited influence of post-entrapment degassing. Melt embayments which are open to the external environment however have significantly lower water concentrations (0.9-2.4 wt.%), although their CO₂ concentrations are indistinguishable from melt inclusions at the crystal cores. Quartz crystals themselves contain 17 ± 4 ppm water, with the infrared spectra revealing charge balance of H⁺ by Al³⁺. Concentration maps show that H₂O is strongly zoned, with progressively less water towards the crystal rim, in contrast to the melt inclusion record. Laser ablation profiles show that Al has a similar concentration distribution, indicating that the H₂O profiles are mainly controlled by the availability of Al in quartz, rather than due to diffusive loss, explaining why the melt inclusions show such limited core-rim variation. Further work will combine these directly measured volatile concentrations with estimates from rhyolite-MELTS modelling and mineral hygrometry, establishing a uniquely detailed view of volatile evolution for the Yellowstone magmatic system.
P 2.37
Thermal perspectives on the diversity and temporal evolution of magma chemistry

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Detailed chemical analyses of single volcanic and plutonic complexes have revealed that some magmatic systems are prone to produce a wide range of compositions, while others sample rather monotonous chemistry through time. It has been suggested that these differences are related to barriers in magma properties like density and viscosity. The reason why such filters would act with large differences in efficiency between neighboring volcanoes remains, however, enigmatic.

We designed a combined thermal and petrological model to explore how magma injection rates are linked to the chemical variability and long-term temporal evolution of mid to lower crustal magma reservoirs. To quantify the possibility of finding magma of a specific chemistry through time, we calculated a weighted average mobile magma composition, which we defined as magma with less than 50% crystals and all the interstitial melt. We find that the average mobile magma chemistry generally evolves in a reversed sense of igneous differentiation from silicic towards more mafic in time. Similar trends are sometimes observed in the plutonic and volcanic rock record, which indicates that they are linked to the incremental assembly of magmatic bodies. Our analysis also shows that the long-term geochemical variability relates to the frequency-size distributions of injections and the thermal state of the crust. High frequency pulses of small batches of magma into relatively hot or deep crustal settings produce tighter chemical variability compared to less frequent but larger recharge events into colder or more shallow environments. Our combined numerical and petrological model provides a framework to link the temporal evolution of magma chemistry in the volcanic and plutonic record to magma fluxes and the thermal architecture of magmatic systems.
Basaltic oceanic crust is subject to extensive fluid-rock interaction soon after its formation. Driven by hot, shallow intrusives, infiltrating seawater is heated and chemically modified by chemical reactions with basaltic wall-rocks. The rocks in turn are pervasively altered to «spilites» consisting of chlorite + albite + quartz + hematite + titanite ± actinolite, commonly with relict augite. Along the discharge path of these convective systems, the fluid is thought to alter pre-existing spilites to «epidosites», i.e. rocks consisting of epidote + quartz + Fe-oxides + titanite. When the fluid reaches the seafloor at focused vents, it may form black smokers, eventually producing volcanogenic massive sulfide (VMS) deposits.

Epidosites have been studied from various ophiolites as well as from recent oceanic settings. They are usually reported from the sheeted dyke complex, but large epidosites also occur in the pillow lavas in the Semail Ophiolite in Oman.

In this study we have used thermodynamic calculations at subseafloor pressures and temperatures to constrain the range in fluid compositions that can produce massive epidosites via metasomatism. Mineral parageneses found at epidosite reaction fronts in combination with reactive-transport modeling further constrained essential fluid parameters such as Ca and Na activities and the pH of the fluid. Additionally, water–rock ratios required for the formation of epidosites could be calculated using the reactive-transport code Flotran. The model ratios are far greater than those proposed in the literature based on isotopic tracers, but they are comparable to those based on hydrothermal experiments. Overall, the modelled results reproduce the changes in mineralogy, whole-rock composition and rock porosity observed in the Semail Ophiolite.
Hydrothermal alteration associated with volcanogenic massive sulfide (VMS) deposits in the Semail Ophiolite, Oman

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High geothermal gradients during the formation of oceanic crust drive deep circulation of seawater and chemical exchange with the rocks along its fluid pathways. If this modified fluid discharges on the seafloor through focused vents, it forms black smokers that may develop into volcanogenic massive sulfides (VMS) deposits. Alteration around the underlying stockwork zone of these deposits is characterized by replacement of the precursor basalt to assemblages of pyrite + quartz + chlorite. Interestingly, the Fe content of this chlorite tends to increase towards the main upflow zone beneath these deposits (Zierenberg et al., 1988). This gradient may shed light on the composition of the upwelling fluid and mixing between this fluid and Mg-rich unmodified seawater. Moreover, understanding this gradient may lead to improved exploration vectoring. One way to map this gradient is via short-wave infrared (SWIR) spectrometry, as the Mg-Fe(OH) SWIR absorption features of chlorite vary dependently with Mg# (Lypaczewski and Rivard, 2018; Neal et al., 2017).

The Semail Ophiolite hosts numerous VMS deposits in its mafic extrusive sequence (Gilgen et al., 2014), and thus represents an excellent opportunity to test for alteration patterns. However, little is known about the structure and footwall alteration of these deposits. To address this, we mapped the lithologies and alteration styles in the pits of previously-mined VMS deposits and sampled the altered footwall basalts. Thereafter we measured SWIR spectra of the chloritised samples using a Portable Infrared Mineral Analyzer (PIMA). We applied a Savitzky-Golay filter (1964) to smooth the SWIR spectra and to obtain precise spectral positions for the Mg-Fe(OH) vibration peak. These positions are then compared to chlorite compositions analysed by electron microprobe to test previously published spectral proxies for composition.

Preliminary results show that two distinct alteration styles exist around the deposits: a proximal alteration with Fe-rich chlorite associated with minor quartz and sulfides, and an overprinting regional alteration with Mg-rich chlorite and albite. The Mg# of these chlorites varies from 0.46 to 0.75 and the corresponding SWIR spectra are shifted by at least 30 nm between the two compositions. Further work will aim to describe the gradient between these composition and fingerprint VMS-related from overprinting chlorite.

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P 2.40

Relationships of banded amphibolites and Ordovician orthogneisses in pre-Variscan basements of the Alps

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Despite of the individual character of each of the pre-Variscan basement units of the Alps, they show analogous formations (paragneisses, migmatites, peraluminous orthogneisses, and amphibolites) and structures indicating similar genetic processes. There is consensus regarding the protoliths of the gneisses and migmatites. But the protoliths of the amphibolites are under discussion because their age is largely unknown and original structures often are overprinted by Variscan and Alpine tectonics. However, the amphibolites (i) are typically banded from millimeter to meter-scale (in all units; e.g., Fig. 1a), (ii) are intercalated with para- and orthogneisses on a map-scale (especially in the Aar massif and Silvretta nappe), (iii) can vary in percentage from 3 area% (Strona-Ceneri zone) to 22 area% (Silvretta nappe), (iv) are associated with metagabbros, meta-ultramafics and (meta-) eclogites (in all units), (v) can be migmatic and occur within migmatite formations (Aar massif).

Most studies interpret the banded amphibolites as members of an ophiolite sequence (due to their MORB signature and association with eclogites and ultramafic rocks) or bimodal metavolcanics (due to their compositional banding). Both tectonic settings are supported by case studies. But from a general perspective of subduction-accretion tectonics of the Ordovician orogeny (Fig. 1b and Zurbriggen 2017) they cannot serve as main setting due to following reasons: A clear ubiquitous ophiolite stratigraphy is lacking and obduction is the exception rather than the rule in accretionary complexes. Furthermore, a rhythmic alteration of acidic and basic layers of volcanic rocks might occur as local phenomenon but is unlikely to explain banded amphibolite formations over geographically large distances.

New field observations from Sassella (Silvretta nappe), Lötschental, Betten, Gletsch (Aar massif), Val Piora (Gotthard nappe), and Molinetto (Strona-Ceneri zone) indicate that the banding of the amphibolites results from a tectono-metamorphic overprint of (i) sets of mafic dykes, (ii) multiple intrusions and intermingling of acidic, intermediate and mafic magmas, (iii) migmatites, and (iv) tectonic mélanges of sediments, mafic and ultramafic rocks.

This large variety of protoliths of banded amphibolites (Fig. 1c) reflects the dynamics in a subduction channel, the overlying mantle wedge and the base of a subduction-accretion complex (Fig. 1d). The mantle underneath large subduction-accretion complexes can be of lithospheric and asthenospheric type and its melting can be induced by fluids and decompression, respectively. As a result, large amounts of basaltic melts intrude the accreted sediments and induce their melting. This produced a similar amount of peraluminous magmas, the cause for widespread acidic Ordovician magmatism in these basement units.

It is proposed that the production of banded amphibolite formations occurs in two major steps. The first step is related to magma interaction processes in the “zone of intermingling” (c. 5-10 km thick) at the base of a subduction-accretion complex (Fig. 1b). There, basaltic melts (and slices of mélangé diapirs containing ultramafics and eclogites) intrude the metagreywackes causing their melting. The solidus of a basaltic melt (c. 900°C; drawn in Fig. 1b) is near to the liquidus of greywacke. Therefore, homogeneous mixing of the two major magmas is unlikely as can be observed in the compositional gap in chemical diagrams. Thus, dyke intrusion and intermingling are major processes, which significantly increase the interface area and resulting heat exchange between crystallizing basaltic melts and cooler metagreywackes and their peraluminous melts (Fig. 1d).

The second step is related to thrusting within the accretionary complex. Similarly as the peraluminous magmas, which intrude syntectonically along steep thrust zones to form sheets of orthogneisses, the intermingled and interlayered mafics are sheared into steep thrust zones and get mylonitized under amphibolite facies conditions. The products are banded amphibolites in all variations. Their spatial association with metagabbros, meta-ultramafics and (meta-) eclogites is due to the intersection of the steep thrust zones with the “zone of intermingling” (Fig. 1b) containing these lithologies as described above (see first production step).
Figure 1. (a) Banded amphibolite from Molinetto (Strona-Ceneri zone; finger for scale). (b) Tectonic setting of an early Paleozoic subduction-accretion complex (Zurbriggen 2017). (c) Scheme of possible protoliths (a-f), which are metamorphosed and mylonitized (red arrows) to result in banded amphibolite. (d) P-T diagram illustrating the two-step production of banded amphibolites in a subduction-accretion complex with peraluminous magmatism.

REFERENCES