2. **Mineralogy, Petrology, Geochemistry**

Francesca Piccoli, Florence Begue, Julien Allaz

*Swiss Society of Mineralogy and Petrology (SSMP)*

**TALKS:**

2.1 Anand A., Pape J., Wille M., Mezger K., Hofmann B.: $^{53}$Cr/$^{52}$Cr model ages of IIAB iron meteorites: implications for accretion and thermal evolution of their parent body

2.2 Chatterjee S., Pandey O.P., Ravindran A., Mezger K., Upadhyay D.: Mafic Dykes from Archean Singhbhum Craton: A Window into the Evolution of Sub-Continental Lithospheric Mantle

2.3 Fontboté L.: Systematic trends in in the evolution of porphyry-related polymetallic deposits


2.5 Hammerli J., Hermann J., Tollan P., Naab F., Spandler C.: In situ CO$_2$ quantification in apatite by FTIR: Opportunities and limitations

2.6 Jorgenson C., Caricchi L., Weber G., Giordano G., Bouvier A., Marxer F., Ulmer P.: Melt inclusions and machine learning – a new approach to the curiosity that is Colli Albani

2.7 Kyas S., Volpatto D., Saar M.O., Leal A.M.M.: Accelerating reactive transport simulations in heterogeneous porous media with Reaktoro and Firedrake


2.11 Weber G., Caricchi L., Arce J.L., Schmitt A.K.: Assessing the state and size of subvolcanic magma reservoirs by thermo-chemical inversion of zircon
POSTERS:

P 2.1 Bach L., Caricchi L., Higgins O., Sheldrake T.: Cluster analysis of crystal zoning: Application to pyroxene megacrystals from the 1669 eruption of Mount Etna

P 2.2 Higgins O., Sheldrake T., Caricchi L.: Quantitative chemical mapping of plagioclase as a tool for the interpretation of volcanic stratigraphy: an example from St Kitts, Lesser Antilles

P 2.3 Ágreda López M., Caricchi L., Jorgenson C., Giordano G., Musu A.: Mildly-explosive to effusive eruptions of Colli Albani (Italy)


P 2.5 Espinel Pachón I.M., de Haller A., Kouzmanov K.: The carbonate-replacement Zn-Pb-Ag Catalina Huanca Mine, Ayacucho, Peru: microthermometry and composition of the mineralizing fluids

P 2.6 Wolf R.C., Diamond L.W.: Seafloor hydrothermal alteration along the downflow pathway: insights from the Semail ophiolite, Oman

P 2.7 Huang P.W., Flemisch B., Qin C.-Z., Saar M.O., Ebibgo A.: Simulation of chemically driven convection in porous media using a charge-balanced multicomponent diffusion model

P 2.8 Nformidah S., Tollan P., Herrmann J.: Metasomatic signatures revealed from trace element concentrations of clinopyroxene

P 2.9 Roodpeyma T., Driesner T.: A re-assessment of the equilibrium constant and aqueous activity ratios for the Albite – K-Feldspar – NaCl(aq) – KCl(aq)

P 2.10 Cisneros M., Behr W.: A global comparison of quartz-in-garnet barometry and conventional thermobarometry


P 2.13 Zakharov D.O., Marin-Carbonne J., Aléon J., Bindeman I.N.: Triple oxygen isotope trend recorded by Precambrian cherts: A perspective from combined bulk and in situ secondary ion probe measurements
2.1

$^{53}\text{Cr}/^{52}\text{Cr}$ model ages of IIAB iron meteorites: implications for accretion and thermal evolution of their parent body

Aryavart Anand*, Jonas Pape*,**, Martin Wille*, Klaus Mezger* & Beda Hofmann*,***

* Institut für Geologie, Universität Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland (aryavart.anand@geo.unibe.ch)
** Institut für Planetologie, Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany
*** Naturhistorisches Museum Bern, Bernastrasse 15, CH-3005, Bern, Switzerland

The IIAB iron meteorites belong to the category of "magmatic irons", and are thought to sample the core of a distinct parent body that experienced large-scale chemical fractionation, most notably metal-silicate separation. The time of metal core formation in the IIAB parent body provides a key time marker for the evolution of early formed planetesimals including the accretion and cooling history of the parent body. The timing and duration of such early Solar System processes, including accretion, differentiation and subsequent cooling, can be investigated using the short-lived $^{53}\text{Mn}^{\text{t1/2}\approx 3.7\text{ Ma}}$ chronometer.

Chromite ($\text{FeCr}_2\text{O}_4$) and daubreelite ($\text{FeCr}_2\text{S}_4$) are the two main carrier phases of Cr in IIAB iron meteorites. Both these minerals have low Mn/Cr ratios ($<0.01$) and thus, preserve the Cr isotope composition of their growth environment at the time of isotopic closure while the in-growth of radiogenic $^{53}\text{Cr}$ from in-situ decay of $^{53}\text{Mn}$ is negligible. Model ages for chromite and daubreelite in IIAB iron meteorites can be obtained by comparing their Cr-isotope composition with the Cr-isotope evolution of the chondritic reservoir, using the known$^1$ abundances of $^{53}\text{Mn}$ and $^{53}\text{Cr}$ at the beginning of the solar system or any point in time thereafter and an estimate$^1$ for the Mn/Cr in the relevant reservoir. In order to systematically resolve the ingrowth of $^{53}\text{Cr}$ over a time span of a very few Myrs, Cr isotope abundances need to be measured with high precision by TIMS.

The isotope ratios do not need any correction for the cosmic ray exposure due to the low Fe/Cr of the samples. Results for chromite from the meteorites Sikhote-Alin and Agoudal and daubreelite from NWA 11420 give an average model age of $\sim1$ Ma after the formation of the Solar System. These ages are in good agreement with the core formation ages in IIAB iron meteorites parent body constrained with the short-lived $^{182}\text{Hf}^{\text{t1/2}\approx 1.7\text{ Gyr}}$ chronometer$^2$. Additionally, the agreement between Hf-W and Mn-Cr ages within uncertainties suggests that both systems closed approximately simultaneously.

REFERENCES


2.2

Mafic Dykes from Archean Singhbhum Craton: A Window into the Evolution of Sub-Continental Lithospheric Mantle

Sukalpa Chatterjee*, Om Prakash Pandey*,**, Arathy Ravindran*, Klaus Mezger*, Dewashish Upadhyay***

* Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland.
** Department of Earth Sciences, Indian Institute of Technology Kanpur, IN-208016, Kanpur.
*** Department of Geology and Geophysics, Indian Institute of Technology Kharagpur, IN-721302, Kharagpur.

Mafic dyke swarms constitute an important marker for reconstructing paleogeographic positions of Archean cratons. In addition, dykes of different ages from the same region can be used to track the temporal geochemical evolution of the subcontinental lithosphere. Of particular interest are dykes and dyke swarms of Archean age, penetrating older Archean crustal nuclei, because of their potential to provide a better understanding of the evolution of Archean mantle composition, mantle dynamics and subsequently the evolution of the continental crust above it. In continental setting, the question mostly revolves around whether the source was sub-continental lithospheric mantle (SCLM), or the upwelling plume or was a mixture of these different sources (e.g. Bartels et al., 2015). However, crustal assimilation during ascent of the magma or post-emplacement metamorphism may potentially alter the primary mantle signature.

The Singhbhum Craton in eastern India is host to at least seven distinct sets of mafic dyke swarms, collectively referred to as ‘Newer Dolerite Dykes’. Present study focuses on four different dyke swarms emplaced between 2.80 and 1.76 Ga. These dykes range from basalt to basaltic-andesite to andesite and have transitional tholeiitic to calc-alkaline affinities. They show intra-swarm geochemical and isotopic (Sr-Nd) heterogeneity and have SiO₂ content mostly > 52 wt.%. The trace elements compositions of these dykes indicate the involvement of a crustal component in their petrogenesis. The dykes have variable but fairly radiogenic ⁸⁷Sr/⁸⁶Sr with gradual increase from oldest to the youngest swarm. They also have sub-chondritic initial ɛNd ranging from -0.9 to -10, which shows gradual less radiogenic signatures in the younger swarms compared to the older ones. This indicates that older enriched material was involved in the petrogenesis of the Newer Dolerite Dykes of the Singhbhum Craton. These dykes have high concentrations of compatible trace elements, which indicate that the parent melts were in contact with mantle peridotite and they did not fractionate much olivine, pyroxene, and magnetite and were not modified by crustal assimilation during ascent and emplacement. The crust-like temporal trend of the Sr and Nd isotopic compositions suggests that the crustal material incubated in the mantle for a long time and was periodically tapped during the dyke emplacement, multiple times between 2.8 and 1.7 Ga.

REFERENCE

2.3
Systematic trends in the evolution of porphyry-related Zn-Pb-(Ag) deposits

Lluís Fontboté*

* Department of Earth Sciences, University of Geneva, 1205 Geneva, Switzerland (lluis.fontbote@unige.ch)

Zinc-Pb mineral deposits in a porphyry system include (i) deposits formed subsequently to a prograde skarn phase, and (ii) replacement bodies and veins that lack skarn assemblages and are best developed in the shallow part of the system, predominantly in the epithermal environment. The latter are frequently called Cordilleran polymetallic deposits, carbonate replacement deposits (CRD), or intermediate-sulfidation (IS) deposits. The term Cordilleran is preferred because these deposits are not restricted to carbonate replacement and often include also low- and/or high-sulfidation mineral assemblages (LS and/or HS).

Based on the study of multiple deposits, an updated model for the evolution of porphyry-related Zn-Pb-(Ag) deposits is presented. It points to a significant overlap between the retrograde stage of Zn-Pb skarns and Cordilleran Zn-Pb deposits. Both mineral deposit groups share characteristics and mineral assemblages that in the ideal case follow systematic trends from low to higher sulfidation state, to subsequently return to lower sulfidation conditions. In Cordilleran polymetallic deposits all or some of the following, frequently telescoped, stages are observed. Repeated events often complicate the picture.

Stage A (LS, Zn-Pb±Cu±Sn, ~350-220°C) is characterized by LS assemblages with pyrrhotite, magnetite, Fe-rich sphalerite (up to 30 mole % FeS), minor galena, chalcopryte and arsenopyrite. Chalcopryte and may be also abundant. In deposits with particularly reduced assemblages, siderite and the Sn-bearing minerals cassiterite, stannite, and herzenbergite occur too and sphalerite may have high In content. Main gangue minerals are quartz and chlorite. When well developed, stage A forms pervasive, massive bodies. In some deposits, stage A is absent or only represented by small pyrrhotite inclusions in stage B pyrite.

Stage B (IS, ~280-200°C) consists predominantly of pyrite, often idiomorphic and coarse-grained, and quartz. Minor wulfenite and gold may occur too. Widespread sericitization indicates pH decrease compared to stage A. This stage frequently overprints stage A; diagnostic features include the formation of cubic, pyritohedral, and octaedric crystals of pyrite and/or replacement of stage A pyrrhotite and arsenopyrite by marcasite and pyrite.

Stage C (HS/IS, ~280-150°C) may reach up to HS conditions developing Cu-Zn±Au assemblages with enargite/famatinite, covellite, Fe-poor sphalerite, galusite, quartz, alunite and kaolinite that grade outwards to IS Zn-Pb-Ag assemblages with Fe-moderate to Fe-poor sphalerite, galena, tennantite-tetrahedrite, bismuthinite, other sulfosalts, chalcopryte, rhodochrosite and other Mn-Fe (±Zn) carbonates as well as ± alabandite. Sericite is present mostly intergrown with Mn-Fe carbonates and quartz. In the outermost zone, barite and hematite are frequent, the later locally replaced by magnetite (mushketovite).

Stage C mineral assemblages occur in veins that may extend laterally for kilometers in detrital, volcanic, and other poorly-reactive rocks, whereas in carbonate rocks stage C may form large replacement bodies and dissolution breccias. In distal parts of stage C veins, stibnite, realgar, orpiment and Ag-bearing minerals may occur. Late calcite ± sphalerite ±galena± arsenopyrite veinlets are common and indicative of further neutralization of the fluid. Anomalous Mn and Fe contents in calcite veinlets are used in exploration as surface and distal expressions of hidden ore bodies. Stage C spans large mineralogical variations; assemblages rich in V, Bi, Ni, Co, In, Ga are also found.

Many Cordilleran Zn-Pb-Ag deposits consist only (or mainly) of stage C with IS mineral assemblages bearing rhodochrosite and other Mn-Fe carbonates. Therefore, in places, they have been termed “intermediate-sulfidation Zn-Pb deposits”. However, it has to be considered that these deposits originate by essentially the same processes forming Cordilleran deposits that also display stages A and B and/or those deposits that develop HS mineral assemblages in stage C. Thus, deposits with only IS assemblages in stage C may constitute the “tail” of larger zoned Cordilleran deposits and of porphyry systems.

In the retrograde stage of Zn-Pb skarns, an evolution that parallelizes that of Cordilleran deposits is often recognized. Most of the ore typically consists of Fe-rich sphalerite in LS assemblages with pyrrhotite and magnetite, siderite, and chlorite, formed at ~ < 350°C that are comparable to the LS stage A described above. Occasionally, the LS stage in Zn-Pb skarns is preceded by chalcopryte-bornite-pyrite assemblages. The LS assemblages are often overprinted by coarse-grained pyrite with a tendency to idiomorphism, like in the Cordilleran stage B. Subsequently, generally minor, veins with Fe-moderate and -poor sphalerite, galena, Ag-bearing sulfosalts, and Mn-Fe carbonates can occur and are equivalent to LS stage C assemblages described above. When these mineral assemblages extend outside the skarn environment, they are...
indistinguishable from Cordilleran bodies. In other words, the evolution from low to higher sulfidation conditions is also observed in Zn-Pb skarns, although here the LS stage is more widespread than in most Cordilleran deposits.

At several Cordilleran deposits, a “pre-A stage” consisting of Mg exoskarn minerals like talc, serpentine, magnetite, siderite, quartz ± less easily recognizable actinolite and tremolite also supports the transition and overlapping between skarn and Cordilleran Zn-Pb deposits. These magnesium-rich assemblages in protoliths devoid of diagenetic dolomite point to previous hydrothermal dolomitization.

The ore stages of both groups of ore deposits have been formed by low- to moderate-salinity magmatic fluids resulting of the ascent, from the porphyry level, of intermediate-density fluids or of brines diluted by magmatic vapor. Direct ascent of magmatic vapor to the Zn-Pb deposition environment also happens and is probably responsible for the extreme acidic and oxidized conditions yielding the alunite-bearing HS mineral assemblages of certain Cordilleran deposits, in part flanking HS Au mineralization. The common tendency from low to higher sulfidation state is generally explained by decreasing temperature and interaction of the mineralizing fluids with host rock. This evolution, followed by buffering by the host rock, is reminiscent of the classical “looping path through time and space” in the porphyry deposit itself.

**This summary is largely based on work in collaboration with members of the Mineral Resources and Geofluids Group of the University of Geneva and the geology staff of several mining companies.**
2.4

Cenozoic magmatic evolution of the Lesser Caucasus and its link with Anatolian and Iranian tectonic belts: Insights from the South Armenian Block - a key witness of crustal growth during Arabia-Eurasia convergence and collision

Marion Grosjean*, Robert Moritz*, Samvel Hovakimyan*, Hervé Rezeau†, Alexey Ulianov**, Massimo Chiaradia*, Rafael Melkonyan***

*University of Geneva, Geneva, Switzerland (marion.grosjean@unige.ch)
**Institute of Geological Sciences, Lausanne, Switzerland
***National Academy of Sciences, Yerevan, Armenia
†Present address: Department of Earth, Atmospheric, and Planetary Sciences, MIT, Cambridge, USA

The South Armenian block (SAB) is located in a key location along the Central Tethyan belt, linking the Turkish and Iranian tectonic and magmatic belts. This study aims at tracking the geodynamic evolution during the convergence and collision of the Arabian plate with the Eurasian margin, and understanding how the SAB has evolved during the subduction of the southern Neotethys beneath Eastern Anatolia and NW Iran.

New geochemistry and geochronology results from this study are complementary to previous work (Rezeau et al., 2016, 2017; Moritz et al., 2016) and hence provide new insights into the regional magmatic evolution in the SAB. The Cenozoic magmatism in the SAB has evolved from calc-alkaline to shoshonitic, both in space and in time, linked to the evolution of the magmatic arc and back-arc. The high-K calc-alkaline to shoshonitic magmatism of the SAB was initiated in the NW and became younger toward the SE, as it migrated closer to the suture zone. Trace element geochemistry of these rocks consistently support an arc-related signature with an enrichment in LILE and depletion in HFSE (Nb, Ta, Ti). Trace element data also indicates that the most potassic magmas are the most metasomatized and were generated by a low degree of partial melting of depleted mantle. According to radiogenic isotopes, the high-K calc-alkaline magmas from the north were sourced by a very juvenile mantle component. It is attributed to asthenospheric mantle upwelling, either during slab retreat or slab tearing in the back-arc. Upwelling of the asthenospheric mantle-derived magma migrated to the SE during late Eocene-early Oligocene slab roll-back/retreat or slab tearing, and mixed with a magma with a higher crustal component. Finally, the late Oligocene-early Miocene period was characterized by adakitic-like magmatism in the SAB (Rezeau et al., 2017; this study) and is attributed to the initiation of the Arabian slab break-off (Rabayrol et al., 2019; this study).

When compared to contemporaneous magmatism in the adjacent tectonic regions, the early to mid-Eocene magmatism of the southern SAB can be linked to the Iranian subduction of the southern Neotethys along the same magmatic arc, especially based on their crustal $^{143}$Nd/$^{144}$Nd(i) ratios. In contrast, during the mid- to late Eocene, the $^{143}$Nd/$^{144}$Nd(i) ratios show that the NW SAB was already in a context of a back-arc setting and was connected to the Eastern Pontides geodynamic evolution, which was the back-arc domain of the Arabian subduction system.

The Oligocene was marked by a magmatic lull in Turkey, which can be attributed to the hard collision of the Arabian plate with the Eurasian margin (Schleißer et al., 2018). In Iran, the collision stage occurred later, with a soft character, thought to be initiated at 36 Ma (Ballato et al., 2011). From mid Eocene to Oligocene, high-K calc-alkaline to shoshonitic magmatism in the NW SAB migrated towards the SE SAB and Alborz magmatic arc (AMA) as a result of slab retreat in a back-arc regime or tearing of the lithosphere.

Finally, the Miocene is characterized by widespread magmatic activity in the Tauride-Anatolian platform, as well as in the Urumieh-Dokhtar magmatic belt. In the SAB and in the northern AMA, this magmatism was restricted to early Miocene and tends to be adakitic in composition, matching in space and time with the start of the Arabian slab break-off underneath Turkey (Rabayrol et al., 2019), which is also reported in Iran (Omrani et al., 2008).

REFERENCES


2.5
In situ CO₂ quantification in apatite by FTIR: Opportunities and limitations

Johannes Hammerli*, Jörg Hermann*, Peter Tollan**, Fabian Naab***, Carl Spandler****

* Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, CH-3012 Bern
(Johannes.hammerli@my.jcu.edu.au)
**Department of Earth Sciences, ETH Zürich, Clausiustrasse 25, CH-8092 Zürich
*** Department of Nuclear Engineering and Radiological Sciences, University of Michigan,
Ann Arbor, Michigan 48109, U.S.A.
**** Department of Earth Sciences, University of Adelaide, Adelaide, SA 5005, Australia

CO₂ is a key agent for metamorphic and igneous processes, for example, driving metamorphic reactions, controlling mass transfer, and impacting the solids. However, determining the CO₂ content in igneous and metamorphic systems is notoriously difficult due to the fugitive behavior of CO₂. While studying fluid inclusions can be a useful way to gain insights into fluid compositions, their complexity can be a limiting factor when interpreting fluid compositions in the crust. An alternative approach for determining crustal fluid compositions is the analysis of minerals that contain volatile fluid tracers. Although several minerals can incorporate the fluid tracers H₂O, Cl, and F, such as amphibole or biotite, the variety of minerals in silicic rocks that host CO₂ is limited. One exception is apatite. Apatite, a ubiquitously present mineral in crustal rocks, can incorporate CO₂ in its crystal structure via different (coupled) substitution (e.g., Pan and Fleet, 2002).

While it has been previously recognized that apatite can incorporate appreciable amounts of CO₂, its quantification on a micrometer-scale has remained difficult due to the lack of suitable techniques, challenging sample preparation methods, and the shortage of reliable standard reference material. Here we present preliminary data from our attempt to calibrate absolute CO₂ contents in apatite on a micro-meter scale using Fourier-Transform Infrared Spectroscopy (FTIR) using a microscope equipped with a Germanium-tip objective. This set up allows attenuated total reflectance measurements ofapatites in polished thin sections, without the need for doubly polished samples. The absorption of C-related bands is calibrated with a set of independently measured apatite standard reference materials via nuclear reaction analyses. Limitations of the technique and new opportunities to better quantify CO₂ contents in igneous and metamorphic systems will be discussed.

REFERENCES
2.6

**Melt inclusions and machine learning – a new approach to the curiosity that is Colli Albani**

Corin Jorgenson*, Luca Caricchi*, Gregor Weber*, Guido Giordano**, Anne-Sophie Bouvier***, Felix Marxer****, & Peter Ulmer ****

* Department of Earth Sciences, University of Geneva, Rue de Maralchaire 13, CH-1205 Genève, (corin.jorgenson@etu.unige.ch)
**Department of Science Geology, Università Degli Stuili Roma Tre, Via Ostiense, 159, 00154 Roma
****Department of Earth Sciences, University of Lausanne, Quartier Mouline, CH-1015 Lausanne
*****Department of Earth Sciences, ETH Zurich, Sonnegestrasse 5, 8092 Zurich

Just 30 km away from Rome sits Colli Albani, a mafic-alkaline volcanic complex that repeatedly produced large volume explosive eruptions, producing up to 63 km$^3$ (DRE). It is uncommon for mafic and alkaline magmas to erupt large volumes in an explosive manner due to the rheological properties of the magma. It is thought that the unusual explosively is related to the addition of CO$_2$ resulting from the interaction with carbonates. However, location of the source carbonates is debated in the literature with some suggesting a shallow carbonate reservoir and others suggesting carbonatic material at the top of the subducted Adriatic plate (Conticelli et al., 2010; Freda et al., 2011). In order to gain insight into the eruptive parameters of this volcano we analyzed melt inclusions, major elements of the phenocrystic phases, and used thermobarometry derived from machine learning. Volatile content of several melt inclusions hosted in clinopyroxene contain >2 wt. % CO$_2$ with values as high as to 3.5 wt. % CO$_2$ and 3.9 wt. % H$_2$O. CO$_2$ solubility studies indicate that such values are not compatible with shallow magma storage. Additionally, clinopyroxene phenocrysts have high magnesium number (up to 0.93) and Cr$_2$O$_3$ content, which suggest equilibrium with the mantle. We used a random forest machine learning approach to determine crystallization conditions of the clinopyroxene phenocrysts and found pressures and temperatures of up to 16 kbar and 1250 °C. The highest pressure and temperature clinopyroxenes are particularly abundant at the base of the ignimbrite outcrop. Thus, we suggest that mafic and CO$_2$-rich magma rapidly ascends from the mantle, destabilizing a shallow crustal magma reservoir and triggering an eruption. We suggest that the high explosively of this system is primarily due to the addition of large amounts of CO$_2$ to the magma in the mantle, which allow for its fast ascent through the lithosphere.

REFERENCES

2.7 Accelerating reactive transport simulations in heterogeneous porous media with Reaktoro and Firedrake

Svetlana Kyas*, Diego Volpatto**, Martin O. Saar*, and Allan M. M. Leal*

* Geothermal Energy and Geofluids (GEG) Group, Department of Earth Sciences, ETH Zürich, Switzerland
(svetlana.kyas@erdw.ethz.ch)
**National Laboratory for Scientific Computing, Brazil

Modeling coupled physical and chemical processes is not only scientifically challenging but also computationally demanding due to the high computing costs of chemical reaction calculations. The importance of reactive transport modeling has significantly increased over the past years due to becoming essential for understanding the processes occurring in surface or subsurface systems as well as engineering and environmental problems for a wide variety of geochemical processes.

Geochemical reaction calculations in reactive transport modeling are costly in general. They become more expensive, the more complex the chemical system and the activity models, used to describe the non-ideal thermodynamic behavior of its phases, are considered. Accounting for many aqueous species, gases, and minerals also contributes to more expensive computations. This work investigates the performance of the on-demand machine learning (ODML) algorithm presented in Leal et al. (2020) when applied to different reactive transport problems in heterogeneous porous media. We demonstrate that the ODML algorithm enables faster chemical equilibrium calculations by one to three orders of magnitude. This, in turn, significantly accelerates the entire reactive transport simulations. The numerical experiments are carried out using the coupling of two open-source software packages: Firedrake (Rathgeber et al., 2016) and Reaktoro (Leal, 2015).

To highlight the critical performance characteristics of the ODML algorithm, we use Figures 1. Here, we summarize the overall number of learnings each simulation run required for different tolerances and activity models. We emphasize that the percentage of smart predictions remains greater than 99.8% with respect to the total number of chemical equilibrium problems in the entire simulation. We also include the lowest and highest speedups in chemical equilibrium calculations throughout all the time steps and the overall speedups in the reactive transport simulations achieved by using the ODML method.

REFERENCES


Figure 1. Summary of the total number of learning operations of the ODML algorithm, the percentage of the smart prediction with respect to the total number of chemical equilibrium calculations, the range of speedups in chemical equilibrium calculations throughout all time steps, and the overall speedups in reactive transport simulations for different tolerances $\epsilon$. **Case I:** numerical modeling of a dolomitization process using the HKF and Pitzer activity models. **Case II:** simulation of the H$_2$S-scavenging process using the Debye-Hückel and the Pitzer activity models.
2.8

Investigating silicon isotope behaviour at small scale using melt inclusions.

Clémence Le Lay*, Anne-Sophie Bouvier*, Martin Guitreau**, Estelle F. Rose-Koga**, Muriel Laubier** & Lukas P. Baumgartner*

*Institut des Sciences de la Terre, Université de Lausanne, Geopolis, Quartier Mouline, 1015 Lausanne (clémence.lelay@unil.ch)
**Laboratoire Magmas et Volcans, Université Clermont-Auvergne, Campus Universitaire des Cézeaux, 6 Avenue Blaise Pascal, 63178 Aubière Cedex

Melt inclusions are considered as representative of mantle derived primitive basaltic magmas when trapped in euhedral Mg-rich olivine crystals (Faure et Schiano, 2005). Despite some post-entrapment processes (e.g., Danyushevsky et al., 2000) the study of these melt inclusions leads to important insights (e.g., mantle source composition, magmatic processes (Schiano, 2003)). They can also be used to study isotopic heterogeneity in the mantle. In this study, we measure silicon isotope in olivine crystals and their hosted melt inclusions (OHMIs) in 3 samples from 2 different locations on the Mid-Atlantic Ridge: FAMOUS and 14° Triple Junction (Normal-MORB and Enriched-MORB respectively). Indeed, to date, only bulk $^{30}$Si have been reported for Mid-Ocean Ridge Basalt (MORB) samples, and they vary within -0.36 to -0.22‰ (Poitrasson et al., 2017). Measurements of $^{30}$Si in OHMIs and their host from MORB can be used to better understand the behaviour of silicon isotope at small scale in magmatic system.

Si values measured in glasses are representative of bulk MORB values, even if this does not suggest boundary layer effect as a possible process for lower Si. Melt inclusions seem to be in equilibrium with their host. Indeed, the Si isotope fractionation between olivine and lower average $^{30}$Si in melt inclusions seem to be in equilibrium with their host. Indeed, the Si isotope fractionation between olivine and lower average $^{30}$Si in melt inclusions can be a useful analytical bias that still need to be identified for SIMS $^{30}$Si measurements in glasses. This requires further investigations.

OHMIs analysed with LA-MC-ICP-MS display consistent $^{30}$Si values between the 3 samples. For the N-MORB, $^{30}$Si values range from -0.32 ± 0.14‰ (2se) to -0.65 ± 0.14‰ (2se) for ARP73-10-03 and from -0.42 ± 0.11‰ (2se) to -0.65 ± 0.11‰ (2se) for CH31-DR8. For the E-MORB, values range from -0.25 ± 0.14‰ (2se) to -0.79 ± 0.12‰ (2se). For the 3 samples, OHMIs record homogeneous $^{30}$Si, but their average value (-0.47 ± 0.17‰ (2sd)) is lower than average MORB glasses from the Atlantic (-0.27 ± 0.06‰ (2sd)) (Savage et al., 2010). Since the 3 basaltic standards used during LA-MC-ICP-MS measurements (BHVO-2, BIR and BCR) gave consistent results with literature (e.g., obtained $^{30}$Si_BHVO-2 = -0.29 ± 0.13‰ (2sd), literature $^{30}$Si_BHVO-2 = -0.27 ± 0.08‰ (2sd)) (Zambardi et Poitrasson, 2010), we suggest that the lower $^{30}$Si measured in OHMIs compared to MORB glasses is real. The 4 host olivine crystals (Fo90) returned an average $^{30}$Si of -0.34‰ ± 0.17‰ (2sd). Despite the apparent typical average $^{30}$Si measured in olivine and lower average $^{30}$Si in melt inclusions, these results will be discussed as a possible tool to investigate silicon isotope fractionation between melt and minerals or during magmatic differentiation.

REFERENCES


Poitrasson, F. 2017: Silicon Isootope Geochemistry, Reviews in Mineralogy & Geochemistry, 82, 289-344.

differentiation, Geochimica et Cosmochimica Acta, 75, 6124-6139.
Schiano, P. 2003: Primitive mantle magmas recorded as silicate melt inclusions in igneous minerals, Earth-Science Reviews, 63, 121-144.
Tissandier, L., & Rollion-Bard C. 2017: Influence of glass composition on secondary ion mass spectrometry instrumental
mass fractionation for Si and Ca isotopic analyses, Rapid Communications in Mass Spectrometry, 31, 351-361.
2.9

The missing magmatic arc and the case for Ampferer-type subduction in the Alps and Pyrenees


* Institute for Marine and Antarctic Sciences, University of Tasmania, 7004 Battery Point, Tasmania
** Institute of Earth Sciences, University of Lausanne, 1015 Lausanne
*** Institute of Geochemistry and Petrology, ETH Zurich, 80092 Zurich
**** Sorbonne Université, CNRS-INSU, Institut des Sciences de la Terre Paris, ISteP UMR 7193, F-75005 Paris
***** GEC, Université de Cergy-Pontoise, Cergy F95000
* School of Earth Sciences, University of Bristol, BS8 1RJ, Bristol
xx Research School of Earth Sciences, Canberra, ACT 2601

In the early 1900s, G. Steinmann and O. Ampferer identified two fundamental characteristics of the Alpine orogen, namely ophiolites (Steinmann Trinity, Steinmann, 1905) and the underthrusting of crustal material at depth ("verschluckung"), or "subduction" (e.g. Ampferer and Hammer, 1911). Ever since these discoveries, the evolution of the Alps, from rifting to ocean spreading, subduction and finally to continental collision has remained controversial.

The geophysical identification of subducting oceanic lithosphere at convergent margins and active mid-ocean ridge spreading in the mid-1900s (e.g. Heezen and Tharp, 1966) enabled the development of the conceptual framework of the motion of rigid oceanic plates as the key driver of Plate Tectonics, which was then implemented in the Alps (c.f. Trümpy, 2001). However, we highlight numerous characteristics of the Alpine and Pyrenean orogens that are fundamentally distinct from typical Wadati-Benioff-type of subduction. Benioff-type subductions have large oceanic slabs, a long term magmatic record and intra-oceanic subduction-initiation signatures during the first 20 Ma of subduction which include upper-plate extension and magmatism followed by either obduction or formation of arc system. Other characteristics include the minor abundances of high-pressure rocks in accretionary prism and near-absence of evidence of (ultra-)high pressure rocks. On the other hand, the Pyrenees and Alps are characterized by amagmatic subduction initiation at passive margins and a pre-collisional lithosphere comprised of rift basins characterized by thinned continental crust, exhumation of heterogeneous subcontinental mantle and oceanic core complexes (e.g. Tricart and Lemoine, 1983). The Pyrenees record no magmatism during convergence, whereas magmatism in the Alps is only recorded during collision (McCarthy et al., 2018). This leave a ca. 50-60 Ma gap in the Alps, from subduction initiation to collision, where the detrital zircon record shows no magmatism even though subduction of oceanic and continental fragments reaches ~2 GPa. Moreover, the Alpine orogen shows abundant high-pressure lithologies and coherent imbrication of high-pressure passive margins and oceanic core complexes (Beltrando et al., 2014).

These discrepancies can be resolved by reintroducing the term of Ampferer-type continental subduction. Convergence was controlled not by spontaneous subduction of rigid oceanic lithosphere but by the forced closure of hyper-extended basins along weakened, serpentinitised passive margins. This allows us to distinguish Benioff-type oceanic subduction resulting from the efficient subduction of oceanic lithosphere, abundant magmatism and limited exhumation of metamorphic lithologies, from Ampferer-type continental subduction, derived from the closure of hyper-extended continental basins, inefficient deep subduction of hydrated (serpentinites and oceanic sediments) lithologies, preservation of high-pressure units and amagmatic characteristics.

Nearly 20 years ago, R. Trümpy published a fascinating paper entitled “Why plate tectonics was not invented in the Alps” which dealt with the evolution of geological thought in the Alpine realm since the inception of the nappe concept in the 19th century. We argue that the reason the Alps were not the prime location to develop a robust Plate Tectonic Theory is precisely because the Alps might be better understood in terms of continental tectonics (Molnar, 1988), namely extreme intracontinental extension, ultra-slow plate separation and compression of mainly hyper-extended continental domains (McCarthy et al., 2020).

REFERENCES
Ampferer, O., & Hammer, H., 1911: Geologisches Querschnitt durch die Ostalper vom Allgau zum Gardasee, Jahrbuch d. k. k. geol. Reichsanstalt. Austria, 61, 631-710.


Molnar, P., 1988, Continental tectonics in the aftermath of plate tectonics: Nature, 335,131–137,


Tricart, P, & Lemoine, M, 1983, Serpentinite oceanic bottom in South Queyras ophiolites (French Western. Alps): record of the incipient oceanic opening of the Mesozoic Ligurian Tethys, Eclogae Geologicae Helvetiae, 76(3), 611–629

Trümpy, R., 2001: Why plate tectonics was not invented in the Alps, Int. J. Earth Sciences (Geol. Rundsch) 90, 477–483.
Mineralization stages at the Ayawilca Zn-Pb-In-Ag-Sn-Cu deposit, Pasco, Peru: new insights.

María Francisca Uzieda*, Lluís Fontboté*, Kalin Kouzmanov*, Matthieu Harlaux**, Diego Benites***, Lisard Torró***, Álvaro Fernández-Baca****

* Department of Earth Sciences, University of Geneva, 1205 Geneva, Switzerland (maria.uzieda@etu.unige.ch)
** Nevada Bureau of Mines and Geology, University of Nevada, Reno, USA
*** Pontifical Catholic University of Peru, Lima, Peru
**** Tinka Resources, Av. Benavides 1579-306, Miraflores, Lima 15084, Peru

The “Cordilleran” Ayawilca Zn-Pb-In-Ag-Sn-Cu deposit is part of the Miocene polymetallic belt of Central Peru (Fontboté, 2018), 40 km northwest of the world-class deposit of Cerro de Pasco. The blind Zn-Sn mineralization occurs mainly as 10 to 30 m-thick lenses (“mantos”) and up to dm-thick veins. Mineralization is largely hosted in limestones of the Upper Triassic to Lower Jurassic Pucará Group that in the deposit area overlie carbonaceous phyllites of the Excelsior Group (Devonian) and are overlain by Lower Cretaceous detrital sedimentary rocks of the Goyllarisquizga Group (Peralta et al., 2019). Zinc-(Ag) veins are also present in the western and eastern parts of the deposit. In the present work, we refine the previously defined paragenetic sequence (Benites et al., 2019) focusing on minerals appropriate for fluid inclusion studies (Fig. 1A). Fluid evolution in terms of sulfidation state is shown in Fig. 1B.

Stage Pre-A consists mainly of Mg-siderite, magnetite, prismatic quartz with undulose extinction (q1 in Fig. 1A), and, frequently in voids, talc and chlorite. Local presence of actinolite-tremolite relicts suggests transition to skarn. This stage is identified in the lower part of the Pucará limestone close to the contact with Excelsior phyllites.

Stage A is the volumetrically most important and consists of a low-sulfidation assemblage with pyrrhotite, quartz, Fe-rich sphalerite (up to 30% FeS), arsenopyrite, chalcopyrite, cassiterite, stannite, herzenbergite and minor apatite (Figs. 1C-E). Several prismatic quartz generations are distinguished. Comb quartz, mainly pre-pyrrhotite, forms up to 10 mm crystals (q2 in Figs. 1A; 1C) on which tips occur pyrrhotite and arsenopyrite inclusions. Milky quartz grains including apatite blebs postdate pyrrhotite (q3 in Fig. 1A; 1E). It is followed by clear zoned quartz (q4 in Fig. 1A). Fluid inclusion studies performed on quartz (q4) from stage A (Harlaux, 2019) yield homogenization temperatures ranging from 341°C to 265°C and salinities between 2.4 and 9.1 wt.% NaCl equiv.-

Stage B consists of marcasite and pyrite altering stage A pyrrhotite and mainly of coarse-grained, partly euhedral pyrite. Unlike at Cerro de Pasco (Rottier et al., 2018), no quartz suitable for fluid inclusion studies is observed in Stage B.

Stage C is poorly developed and made up of Mn-Fe carbonates (partly banded), intermediate- to low-Fe sphalerite (10-2% FeS), galena, chalcopyrite, bismuthinite, native bismuth, fahlore, Pb-Ag sulfosalts, kaolinite, dickite, and muscovite, outlining an intermediate sulfidation state. Minor arsenopyrite occur too. Small (up to 15 µm) negative crystal-shaped two-phase (liquid-vapor) fluid inclusions have been observed in growth zones of the Mn-Fe carbonates.

This study was economically supported by the Peruvian CONCYTEC-FONDECYT-World Bank project 107-2018-FONDECYT-BM-IADT-AV

REFERENCES


Harlaux, M. 2019: Fluid inclusion study of the early pyrrhotite mineralization stage from the Ayawilca Zn-In-Ag-Sn deposit, Peru. UNIGE, 22 p, (unpubl.)

Figure 1. A) Paragenetic sequence of the Ayawilca deposit modified from Benites et al. (2019). B) Schematic representation of stages A, B, and C in a modified log fS2 vs temperature diagram of Einaudi et al. (2003) based on stable sulfide mineral assemblages; red lines indicate FeS (mol%) contents of sphalerite (Barton & Toulmin, 1966); starting temperature of stage A based on Harlaux (2019). C) Stage A vein, red arrow indicates quartz growth direction. D) Cavity in pyrrhotite filled with cassiterite, stannite, and arsenopyrite. E) Stage A pyrrhotite altered to marcasite (stage B) and crosscut by stage C Mn-Fe carbonate. asp: arsenopyrite; cst: cassiterite; cpy: chalcopyrite; hrz: herzenbergite; mrc: marcasite; po: pyrrhotite; qz: quartz; st: stannite.
2.11

Assessing the state and size of subvolcanic magma reservoirs by thermo-chemical inversion of zircon

Gregor Weber*, Luca Caricchi *, José L. Arce** & Axel K. Schmitt***

*Department of Earth Sciences, University of Geneva, Rue des Marîchers 13, CH-1205 Geneva (gregor.weber@unige.ch)
**Instituto de Geología, Universidad Nacional Autónoma de México, Coyoacán, MEX-04360 Ciudad de México
***Institut für Geowissenschaften, Universität Heidelberg, Im Neuenheimer Feld 235, D-69120 Heidelberg

Determining the current state and size of magma reservoirs is crucial to mitigate volcanic hazards. However, the spatial resolution of geophysical imaging techniques is often too low to fully assess the volume of eruptible magma stored in the system, and the eruptive history of a volcano through geological and geochemical records does not resolve the present day state of the subvolcanic plumbing system. We developed and applied a new technique based on zircon geochronology, trace element geochemistry and thermal modelling to Nevado de Toluca volcano in Mexico to estimate the rate of magma input and accumulation of potentially eruptible magma in the subvolcanic reservoir. Our calculations constrain the average rate of upper crustal magma recharge to values between $5.8 \times 10^{-6}$ and $7.5 \times 10^{-6}$ km$^3$ km$^{-2}$ yr$^{-1}$. We also show that only a few percent of the supplied magma erupted and that a maximum melt volume of $\sim 350$ km$^3$ is potentially stored within the upper crustal plumbing system of the volcano today. The presence of eruptible magma at Nevado de Toluca is transiently associated with recharge events over timescales of years to centuries. We emphasize that dormant stratovolcanoes, such as Nevado de Toluca, may transition into unrest and eruption over short periods of time potentially without geophysical evidences for melt-rich magma bodies in the shallow crustal storage region. This calls for the need to extend monitoring networks and to combine multiparametric monitoring with petrology and modelling to gather a quantitative understanding of the current status of dormant volcanoes. Our approach can be widely applied and provides vital quantitative information to better assess the potential magnitude of future volcanic eruptions.
P 2.1

Cluster analysis of crystal zoning: Application to pyroxene megacrystals from the 1669 eruption of Mount Etna

Loris Bach*, Luca Caricchi*, Oliver Higgins*, Thomas Sheldrake*

* Department of Earth Sciences, University of Geneva, Rue des Maraîchers 13, CH-1205 Genève

Chemical zoning of minerals provides information on the magmatic processes preceding volcanic eruptions (Caricchi et al. 2020). Here we use cluster analysis to objectively and quantitatively study chemical zoning and identify the processes responsible for one of the large and disruptive eruptions of Mt Etna. We analysed 31 pyroxene megacrystals from the 1669 eruption of Mount Etna (Monti Rossi). The crystals have been cut perpendicular to the c-axis, polished, mounted in epoxy and then scanned with an electron microprobe at the University of Geneva. Compositional maps for silicon, calcium, magnesium, aluminium and chromium were collected. These crystals present both concentric and sector zoning. We use the intensity of the signals for each element to identify chemical clusters using cluster analysis. This is an unsupervised learning technique and consequently no prescribed number of clusters exists. Thus choosing the correct number of clusters is one of the most important challenges to apply this method. The initial target of the study is to identify the best methods to obtain compositional clusters which make petrographic and geochemical sense. To reach our goal, different algorithms have been applied using the R programming language. The two principal methods are the K-means (Hartigan-Wong) algorithm and the Ward’s minimum variance method for hierarchical clustering. Both are working and widely applied techniques but need to be adapted to perform better with overlapping chemical data from a single mineral. The choice of the number of clusters remains a problem since none of the many tested indexes give satisfying results for each crystal. Therefore, we will design a new method or a combination of methods that gives the best results. To estimate the performance of the algorithms we will design a statistical test with elemental maps that will be visually assessed by geology and mathematics students.

We will present the preliminary results of our study and some applications to the Monti Rossi eruption.

REFERENCES
P 2.2

Quantitative chemical mapping of plagioclase as a tool for the interpretation of volcanic stratigraphy: an example from St Kitts, Lesser Antilles

Oliver Higgins*, Thomas Sheldrake*, Luca Caricchi*

*Department of Earth Sciences, University of Geneva, Rue de Maraîchers 13, CH-1205 Genève (Oliver.Higgins@unige.ch)

Establishing a quantitative link between magmatic processes operating at depth and volcanic eruption dynamics is essential to forecast the future behaviour of volcanoes, and to correctly interpret monitoring signals in active systems. The study of chemical zoning in minerals can be exploited for such a purpose due to its ability to fingerprint successive events or states within a magmatic system as the crystals grow. However, to move beyond a qualitative understanding of a magmatic system an unbiased quantification of a large number of zoned crystals is required. We apply an image segmentation approach to thin section scale chemical maps to segment textural zones in plagioclase and correlate these zones between crystals from a stratigraphic sequence from St Kitts, Lesser Antilles. Mapping crystals at the thin section scale allows us to assess chemical and textural complexity within an individual sample and between different samples. By working on a stratigraphic sequence with this methodology we can quantify chemical and textural complexity in time, in this case specifically on a millennial timescale.

Furthermore, recurring zoning patterns observed from this "crystals-eye view" of the magmatic system have the potential to show temporally repetitive processes experienced by the magma at depth. When coupled with textural quantification, these data show that variations in whole-rock geochemistry are more likely due to subtle variations in the assemblage of recycled phenocrysts, rather than long-term variations in chemistry of the juvenile magma. The evolution of microlite chemistry unveils a temporal trend towards less chemically evolved magma.
P 2.3

Mildly-explosive to effusive eruptions of Colli Albani (Italy)

Mónica Ágreda López*, Luca Caricchi*, Corin Jorgenson*, Guido Giordano**, & Alessandro Musu*

*University of Geneva, rue des Maraîchers 13, Geneva CH-1205, Switzerland.  
(Monica.Agreda@etu.unige.ch)

**Dipartimento di Scienze Geologiche, Università degli Studi di RomaTre, Largo S. Leonardo Murialdo, 1, 00146, Roma, Italy.

The Colli Albani volcano is located about 30 km SE of Rome and is part of the Roman Magmatic Province along the NW-SE extensional Tyrrenian margin of Italy (Marra et al. 2004). Colli Albani has been active since c. 600 ka displaying a range of eruptive styles from caldera-forming to plinian explosive paroxysms and mildly explosive-effusive eruptions. All erupted products are mafic and potassic (Giordano & CARG Team 2010).

This project focus on the understanding of the processes that lead to such a variety of eruptive behaviours involving mafic-alkaline magmas. We combine physical volcanology, petrology, and geochemistry and focus on one of the mild-explosive to effusive units: the Fontana Centogocce formation.

The Fontana Centogocce formation (SLV) is constituted of fall deposits, lava flows and pyroclastic deposits that are located stratigraphically between the Pozzolane Nere (407 ± 4 ka)(Karner et al. 2001) and the Villa Senni ignimbrites (351-357 ±3 ka) (Karner et al. 2001) (Giordano & CARG Team 2010).

We are collecting whole rock analyses, mineral chemistry analyses and performing a detailed petrographic study to compare the units constituting the Fontana Centogocce formation and an existing dataset for the Villa Senni ignimbrites. We will use unsupervised and supervised learning approaches to identify similarities and differences between large caldera-forming eruptions and mild-explosive to effusive activity of the Colli Albani volcano and attempt to constrain the processes responsible for these different eruptive dynamics.

REFERENCES


P 2.4

Investigation of the thermo-chemical evolution of magma reservoirs through the growth and the analysis of experimentally zoned crystals

Alessandro Musu 1, Luca Caricchi 1, Diego Perugini 2, Rosa Anna Corsaro 3, Francesco Vetere 2, Maurizio Petrelli 2

1 Department of Earth Sciences, University of Geneva, Rue des Maraîchers 13, CH-1205 Geneva, Switzerland
2 Department of Physics and Geology, University of Perugia, Piazza dell’Università, 1, 06123 Perugia, Italy
3 Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Etneo-Sezione di Catania, Catania, Italy.

Magma reservoirs are characterized by thermo-chemical gradients that lead to large variations of the physical properties of the magma they contain. Magmatic minerals can record this physico-chemical variability within a magma reservoir, recording variations of intensive parameters as chemical signals. To better understand these chemical signals, we use an experimental approach to grow chemically zoned minerals under controlled conditions. This allows us to study the role of intensive parameters, element diffusion and mineral growth on the chemical zoning. The starting materials for our experiments are natural samples of tephra collected from 2002-03 Mt. Etna eruption. Chemical zonation is forced by oscillating the temperature inside a high-temperature furnace under three different regimes: static conditions, using a controlled deformation gradient (concentric cylinder apparatus) and using a chaotic mixing regime (Chaotic Magma Mixing Device – CMMD).

We measure both major and trace elements distribution maps on a large number of crystals using Electron Probe Micro Analyzer (EPMA) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), respectively. Using a series of custom-built machine learning algorithms we disentangle zoning patterns related to variations of the thermodynamic conditions of crystal growth from those produced by the competition between diffusion and growth. Backscattered Electron (BSE) images of the sample are also analyzed for Crystal Size Distribution (CSD). The main aims of this project are to provide experiments that will help deciphering the chemical signals recorded in magmatic minerals and to improve our understanding of magma reservoir dynamics.
P 2.5

**Mineralizing fluids in the Catalina Huanca carbonate-replacement Zn-Pb-Ag deposit, southern Peru**

Iván Mateo Espinel Pachón *, Antoine de Haller *, Kalin Kouzmanov *

*Department of Earth Sciences, University of Geneva, Rue des Maraîchers 13, 1205 Geneva, Switzerland
(Ivan.Espinel@etu.unige.ch)

Catalina Huanca is a medium-sized carbonate-replacement (Zn-Pb-Ag) deposit located in the Andean Cordillera of southern Peru, 400 km southeast of Lima, and 100 km south of Ayacucho (unpublished company reports; Dávila et al., 2012). The Catalina Huanca mineralization is located at the base of a major Tertiary eastward thrust and consists of veins and replacement bodies. It is controlled by a NE trending horsetail fault structure cutting the foreland Tertiary red beds (previously attributed to the Permo-triassic Mitu Group; Davila et al., 2012) and the overthrusted Pucara Group limestones. Spacially associated pre-ore igneous rocks include rhyolitic and trachytic dikes.

Mineralization at Catalina Huanca comprises seven stages with contrasting mineralogy. Stage I corresponds to the high-temperature skarn replacement, with biotite and subordinate diopside, pyroxmangite, andradite, and ilvaite. It is followed by stage II, with high-temperature hematite replaced and overgrown by magnetite (mushketovite). Stage III consists of adularia, and abundant euhehedral pyrite and quartz with minor arsenopyrite, while stage IV is dominated by Fe-rich sphalerite with chalcopyrite disease in part replacing the early pyrite. Stage V is characterized by early fluorite associated with hematite, quartz, Fe-poor sphalerite, fahlore, enargite, chalcopyrite, and galena. Stage VI corresponds to the epithermal evolution of the system, with abundant siderite-rhodochrosite as replacement and open space fillings, followed by kaolinite. Finally, stage VII is characterized by the presence of carbonates (subhedral or muddy facies) and minor apatite.

The goal of the present study is to characterize the mineralizing fluids and their evolution. A large number of samples (>50) has been used to define the paragenetic sequence of the mineralization. Of these, about fifteen key mineralized samples were selected from Stages III and IV for fluid inclusion analyses in ore and gangue minerals, combining traditional microscopy with near-infrared (NIR) microscopy and microthermometry. This approach allows tracing the hydrothermal fluid evolution and the P-T-X conditions of ore formation.

The paragenetic sequence is presented in Figure 1, and the ongoing work includes fluid inclusion analysis in different generations of sphalerite and fluorite (Fig. 2). Abundant primary and secondary L-V inclusions are found in sphalerite (early and late), but only secondary inclusions in fluorite. First results on fluorite show Th ranging from 150° to 250°C and salinities from 8 to 11 wt% NaCl eq. Further studies will include microthermometry measurements on sphalerite-hosted inclusions, cathodoluminescence petrography, electron microprobe analyses of sphalerite, Raman spectroscopy and LA-ICP-MS analyses of individual fluid inclusions in gangue and ore minerals.

REFERENCES
Figure 1. Paragenetic sequence of the Catalina Huanca deposit. Red arrows indicate minerals used for the fluid inclusion study.

Figure 2. a) Negative crystal-shaped primary fluid inclusions in Fe-rich sphalerite (NIR light); b) Secondary fluid inclusions on fluorite. c) Primary fluid inclusions in Fe-poor sphalerite trapped along a twin plane.
Seafloor hydrothermal alteration along the downflow pathway: insights from the Semail ophiolite, Oman

Robin C. Wolf & Larryn W. Diamond

Institute of Geological Sciences, University of Bern, Balzerstrasse 3, CH-3012 Bern (robin.wolf@geo.unibe.ch)

Hydrothermal alteration is ubiquitous throughout oceanic crust. Induced by subseafloor seawater circulation near mid-ocean ridge (MOR) spreading centres, alteration influences ocean chemistry and it leads to formation of Volcanogenic Massive Sulfide (VMS) deposits at black smoker vents. Our current understanding of seafloor alteration has largely been obtained from ocean drilling of in-situ oceanic crust, experimental fluid–rock studies, and examination of oceanic crust in ophiolites. Comparisons between ancient ophiolite and ‘modern’ MOR settings can be made as they share similar crustal stratigraphy, the hydrothermal agent is seawater, and the presence of disequilibrium assemblages is common (Lippard et al., 1986).

While research on seafloor processes has begun to understand the evolution of the hydrothermal system over space and time, and to clarify the recharge and discharge pathways, the absolute timing of mineral formation and the element budgets and fluxes for each of the alteration stages/processes remain unclear.

Our ongoing study aims to unravel the complex hydrothermal alteration history of the Semail ophiolite and reconstruct the water–rock interaction along the downflow pathway by analysing representative stratigraphic transects across the Semail crust. With petrographic analysis, including optical microscopy, Raman spectroscopy and scanning electron microscopy, we show the changes in mineralogy and geochemistry across each transect, the paragenetic sequences of alteration reactions, and compare these observations with the hydrothermal alteration histories of the modern ocean crust and other ophiolites.

Generally, hydrothermal alteration along the downwelling zone of modern oceanic crust and ophiolites is similar; both the upper sheeted dykes and the volcanic sequence are pervasively altered to various intensities, and alteration ‘grade’ increases with increasing stratigraphic depth. However, many differences exist between ophiolites and oceanic crust, and between ophiolites themselves (Fig. 1). These differences may be a result of single versus multiple periods of magmatic activity, superimposition of regional metamorphic effects in the ophiolites, and/or longer lived hydrothermal circulation in certain ophiolites due to sediment capping (Alt, 1996; Alabaster & Pearce, 1985).

The Semail ophiolite ranks as one of the most intensely altered examples of oceanic crust anywhere, as testified by its rarity of fresh glass, its complete or near-complete alteration of the extrusive section to sub-greenschist to greenschist facies spilites, and its lack of very low temperature alteration assemblages, which are common in in-situ oceanic crust (Alabaster & Pearce, 1985; Pflumio, 1991). A remarkable feature is the stability of hydrothermal chlorite through to the very top of the Semail crust. Thus, the secondary mineralogies along the downflow pathway of the Semail ophiolite presumably reflect a complex, multistage hydrothermal alteration history. Nevertheless, the density of known VMS deposits in the ophiolite is no higher than in other more weakly altered ophiolites, such as Troodos.

Figure 1. Distribution of secondary minerals in the Semail and Troodos (Cyprus) ophiolites, and Integrated Ocean Drilling Program (IODP) drill hole 504B. Scale indicates depth (km) below sediments. Vertical lines indicate occurrence of the mineral (solid = ubiquitous, dashed = locally present). Sme = Smectite; Chl-Sme = Chlorite-Smectite; Cel = Celadonite; Zeo = Zeolite; Prh = Prehnite, Pmp = Pumpellyite; Qtz = Quartz; Chl = Chlorite; Alb = Albite; Ep = Epidote; Act = Actinolite; Cal = Calcite. Modified from Alt et al. (1996), Pflumio (1991), Gillis & Robinson (1990), and Alabaster & Pearce (1985).
REFERENCES
P 2.7

Simulation of chemically driven convection in porous media using a charge-balanced multicomponent diffusion model

Po-Wei Huang*, Bernd Flemisch**, Chao-Zhong Qin***, Martin O. Saar*, Anozie Ebigbo*****

*Geothermal Energy & Geofluids Group, Institute of Geophysics, ETH Zurich, Sonneggstrasse 5, CH-8092 Zurich, Switzerland (powei.huang@erdw.ethz.ch)
**Department of Hydromechanics and Modelling of Hydrosystems, Institute for Modelling Hydraulic and Environmental Systems, University of Stuttgart, Pfaffenwaldring 61, 70569 Stuttgart, Germany (bernd.flemisch@iws.uni-stuttgart.de)
***State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, China (chaozhong.qin@gmail.com)
****Hydromechanics Research Group, Faculty of Mechanical Engineering, Helmut Schmidt University, Holstenhofweg 85, 22043 Hamburg, Germany (ebigbo@hsu-hh.de)

Reactive transport in porous media typically comprises multiply charged ionic aqueous species. According to Joekar-Niasar et al. (2019), the effect of charged transport in porous media is often neglected in reactive-transport models even though it may be relevant. Tournassat et al. (2020) investigated numerical methods of solving the Nernst-Planck equation, including the chemical activity terms, and mentioned that only PHREEQC (Parkhurst and Appelo, 2013) could model such effects. The effect of chemical activity cannot be neglected at high ionic strengths. Such concentrated solutions are common in natural environments such as karstic aquifers or geothermal reservoirs. Therefore, we implement a charge-balanced multicomponent diffusion model using FEniCS (Alnæs et al., 2015) and Reaktoro (Leal et al., 2017) to better understand natural porous systems.

We benchmark our code implementation using an experiment of chemically driven convection in a Hele-Shaw cell (Almarcha et al. 2010). The experiment’s initial conditions consist of an aqueous HCl solution placed on top of an equimolar aqueous NaOH solution. When the barrier between the acid and base is removed, the species starts diffusing, triggering an acid-base reaction, then convecting due to density differences brought about by the reaction. This experiment showcases how complicated coupled transport and reactive processes can be. We model the system using the disassociated ionic species (H+, Cl-, Na+, OH-). Concentration-dependent diffusion fluxes are calculated using the Nernst-Planck model under charge-balanced conditions (Steefel et al., 2015; Alt-Epping et al., 2018). No parameter fitting is necessary. Only measured (well-known) diffusion coefficients at infinite dilution are used. We use Darcy’s law to model density-driven flow in the Hele-Shaw cell. Our simulations are capable of reproducing the complex flow and transport mechanisms seen in the experiments; mechanisms that are triggered by the differences in diffusivity of the various ions.

Figure 1. Simulation of chemically-driven convection. The colors represent the mass fraction of hydrogen ion.

REFERENCES

1-10.


Tournassat, C., Steefel, C.I. & Gimmi, T. 2020: Solving the Nernst-Planck Equation in Heterogeneous Porous Media with Finite Volume Methods: Averaging Approaches at Interfaces, Water Resources Research, 56(3).
Metasomatic signatures revealed from trace element concentrations of clinopyroxene

Siggy Nformidah*, Peter Tollan** & Jörg Hermann*

* Institut für Geologie, Universität Bern, Baltzerstrasse 1+3, 3012 Bern (ndah.nformidah@geo.unibe.ch)
** Institute of Geochemistry and Petrology, ETH Zürich, Zürich, Switzerland

Periodic CO₂ outgassing from volcanoes along the Cameroon Volcanic Line is poorly understood.

The CO₂ could be mantle derived through ancient subduction-related metasomatism during the Pan-African orogeny or be realted to more recent plume-related carbonatite metasomatism. In order to understand these processes, major and trace element concentrations of three representative clinopyroxene-bearing spinel xenoliths (Ka1, Ka2 and Ka7) from the Kapsiki plateau were measured. The Kapsiki plateau shows the oldest volcanism (35-27 Ma) along the line, and also bears the northernmost known occurrence of mantle xenoliths. These xenoliths are quite peculiar because they show records of an ancient depleted mantle which has so far only been reported in the oceanic part of the line. However, with extended volcanism during the Cenozoic and a speculated juvenile state of the lithospheric mantle such features are not expected to be preserved. In this context, these xenoliths are a key to understanding and deciphering the evolution of the SCLM below the rest of the line.

The Kapsiki xenoliths show evidence of melt depletion along with a complex metasomatic history. The Mg# of olivine (0.91-0.92) and orthopyroxene (0.92-0.93), low Al₂O₃ (0.02-2.31 wt.%) contents in orthopyroxene and low incompatible trace elements point to a mantle composition with highly refractory components. Additionally, modal proportions and REE concentrations show that the SCLM has experienced modal and cryptic metasomatism. Modal metasomatism is indicated by the presence of two groups of clinopyroxenes; a low (18.65-18.92 wt. %) CaO group in Ka1 and high (20.62-22.57 wt. %) CaO group which occurs in all samples.

Primitive mantle normalised trace element patterns of ortho- and clinopyroxenes show strong progressive enrichments in LREEs and to a lesser extent MREEs and HREEs in sample Ka1. Clinopyroxene patterns show negative Ti and Nb anomalies and a positive Sr anomaly which indicates the absence of subduction-related metasomatism. Negative Ba and Nb anomalies are inconsistent with metasomatism by alkaline melts. Instead, such features combined with strong enrichments in U and Th indicate the involvement of a carbonate fluid component. The Kapsiki xenoliths thus show evidence for multiple metasomatic events since the trace element patterns do not show any distinctive features which could be attributed to a single melt/fluid type. Furthermore, the composition of the fluid/melt that metasomatised sample Ka1 is different from the others and shows three groups of compositions.

Different systematics were developed to discriminate between different types of metasomatism. Ti/Eu vs (La/Yb)ₙ ratios are used to discriminate silicate and carbonatite metasomatism and show that the low Ca group of Ka1 clinopyroxene with high (La/Yb)ₙ ratios and low Ti/Eu was affected by carbonatite metasomatism. However, the high Ca group along with most of the Ka2 and Ka7 clinopyroxenes with high (La/Yb)ₙ and high Ti/Eu do not show well defined trends and could be a result of the presence of both fluids in varying proportions or a gradual overprinting of one fluid type by another. A few Ka2 and Ka7 grains which show low (La/Yb)ₙ and high Ti/Eu ratios are indicative of interactions with basaltic melts. Zr/Hf vs Ti/Eu, data show that the Kapsiki xenoliths have been metasomatised by carbonated silicate melts and silicate melts which correlates quiet well with results from the Ti/Eu and (La/Yb)ₙ ratios. Ti/Sr ratios of Ka1 samples range from 1-11, Ka2 and Ka7 ratios are much higher in the range of 9-18. Clinopyroxenes with low values (1-5) in sample Ka1 are identical to other clinopyroxenes that have been metasomatised by carbonatite melts with equally low Ti/Sr ratios. Most of the Kapsiki samples also show Ca/Al values of 4-7 which is, consistent with metasomatism induced by volatile rich melts.

Temperatures calculated using the two-pyroxene thermometry gives higher temperatures (1150 °C) for the low CaO clinopyroxene which show carbonatite metasomatism and lower temperatures (880 °C) for the high CaO clinopyroxenes. Our study shows that the SCLM below the kapsiki underwent partial melting with the extraction of basaltic melts, the lower temperatures clinopyroxene records the earliest metasomatism which was of silicate to silicate-carbonatite type and could be be a precursor of the eruption. Clinopyroxenes with the higher temperatures show evidence for carbonatite metasomatism, which could be a potential source of the CO₂ released along the CVL.
P 2.9

A re-assessment of the equilibrium constant and aqueous activity ratios for the Albite – K-Feldspar – NaCl\(_{(aq)}\) – KCl\(_{(aq)}\)

Taraneh Roodpeyma*, Thomas Driesner*

*Department of Earth Sciences, Swiss Federal Institute of Technology Zürich, Zürich, Switzerland
(taraneh.roodpeyma@erdw.ethz.ch)

Thermodynamic properties of solutes in water at temperatures higher than the critical point and at low to moderate densities are crucial to understand chemical fluid-rock interaction in important environments such as mid-ocean ridge, hydrothermal systems, superhot geothermal systems, magmatic-hydrothermal ore-deposits and others. However, at present, we are still lacking sufficient experimental data and a comprehensive thermodynamic formalism to be able to perform accurate geochemical modeling under these conditions.

Among the most important reactions are those between feldspars and aqueous chloride solutions. Accordingly, the reaction

\[
\text{Albite} + KCl_{(aq)} = \text{K-feldspar} + NaCl_{(aq)}
\]

has repeatedly been studied (e.g., Lagache & Weisbrod 1977; Hemley 1967; Orville 1963).

In preparation for a new experimental campaign, we re-assessed those existing data and found that in the derivation of equilibrium constants from the raw experimental data some important effects were not properly taken into account. Namely, the re-assessment shows a significant density-/pressure-dependence of the equilibrium constant and highlights that the activity coefficient ratio of the aqueous species varies strongly with concentration from dilute conditions through the liquid+vapor (L+V) coexistence field into highly saline brine.

The re-assessment is primarily based on the data of Lagache & Weisbrod (1977) and we found that most of their experimental data points were obtained in the L+V region with >90% of the aqueous chloride residing in the liquid phase (Fig.1). This means that the post-quench measured fluid KCl/NaCl ratios were entirely dominated by the high-salinity liquid phase. The nearly constant KCl/NaCl ratio at a given temperature and pressure is, therefore, an artifact of repeatedly measuring the liquid phase composition at L+V conditions although the bulk chloride concentration in the experiments varied of wide ranges.

We re-derived KCl/NaCl ratios for the liquid and vapor phases and found that the vapor phase KCl/NaCl ratio is always significantly lower than that in the liquid phase. The difference may reach a factor of 4 to 5 (albeit with significant uncertainty) at the lowest experimental pressure and diminishes at higher pressures. Taking the vapor KCl/NaCl ratio as the closest proxy to the true equilibrium constant, we could derive the activity coefficient ratio for the two aqueous chlorides as a function of concentration (Fig.2).

We conclude (1) that the currently accepted, pressure-independent equilibrium constant is only valid for highly saline solutions and when ignoring activity coefficients, (2) that the currently accepted equilibrium constants may be in significant error when more dilute solutions are encountered, such as in porphyry-copper style magmatic-hydrothermal systems, and (3) that the assumption of similar or even equal activity coefficients for different electrolytes under the conditions of interest is not valid.

REFERENCES

Driesner, T., & Heinrich C.A. 2007: The system H2O-NaCl. Part I: Correlation formulae for phase relations in temperature-pressure-composition space from 0 to 100 °C, 0 to 5000 bar, and 0 to 1 XNaC, Geochim Cosmochim Acta, 71, 4880-4901.


Figure 1. The most comprehensive experimental dataset is available from the study of Lagache & Weisbrod (1977). The plot illustrates that the data are mostly in the two-phase liquid+vapor region and there is a lack of data in very dilute solutions (=vapor); the dashed and solid curves are representing the L+V coexistence curve, according to Sourirajan & Kennedy (1962) and Driesner & Heinrich (2007), respectively.

Figure 2. The activity coefficient ratios of alkali chlorides, calculated from Lagache & Weisbrod (1977) experimental data, plotted versus the corresponding total chloride molality to show the deviation from unity.
P 2.10

A global comparison of quartz-in-garnet barometery and conventional thermobarometry

Miguel Cisneros* & Whitney Behr*

*Geological Institute, ETH Zurich, Sonnegstrasse 5, CH-8092 Zurich (miguel.cisneros@erdw.ethz.ch)

In recent years, elastic thermobarometry has gained wider acceptance and utility within the petrologic community and beyond. In particular, quartz-in-garnet (qtz-in-grt) elastic barometry is widely used because of the ubiquity of garnet in metamorphic rocks. The technique is based on measuring strain recorded by inclusions, and modeling the elastic evolution of the inclusion-host pair to constrain the initial conditions of inclusion entrapment. Recent studies have experimentally validated the technique by comparing pressures from the qtz-in-grt barometer with experimental conditions of garnet growth and entrapment of quartz, and have shown that the barometer can provide reliable pressure conditions of garnet growth. However, current experimental studies fail to capture the reliability of the technique under disparate pressure (P), temperature (T) and deformation conditions, and studies that systematically compare qtz-in-grt barometry and conventional thermobarometry are sorely lacking.

In this work, we compare P conditions from qtz-in-grt barometry and conventional thermobarometry from the following locations: spatially and temporally variant high P/T subduction zone eclogite blocks from the Franciscan Complex in California, high P/T subduction zone rocks of varying compositions from Syros, Greece, high P/T and low P/T rocks of varying compositions from the Betics system in Spain, and low P/T schists from the Jajarkot and Karnali klippen in the Himalaya. Qtz-in-grt barometry constraints from the Franciscan and Syros show good agreement with some reference P-T conditions, but often disagree with thermodynamic equilibria constraints and subsets of multi-mineral thermobarometry calibrations. Measurements of samples from other localities are currently in progress. This set of quartz inclusion analyses further allows us to evaluate the effects of inclusion geometry, anisotropy, P and T conditions of garnet growth, and P and T paths on the ultimate P conditions recorded by the qtz-in-grt barometer. The data-set also provides insights into the possible limitations of other techniques (e.g., conventional thermobarometry).
Origin and chemical evolution of eclogites and metagabbros in the Münchberg Massif, Germany


*Unit of Earth Sciences, Department of Geosciences, University of Fribourg, Chemin du Musée 6, 1700 Fribourg (johannes.pohlner@unifr.ch)
**GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Schlossgarten 5a, 91054 Erlangen
***Department of Earth Sciences, University of Geneva, Rue des Maraîchers 13, 1205 Genève

The Münchberg Massif (German Bohemian Massif) is an allochthonous nappe pile within the Saxothuringian zone of the Variscan orogen. Its uppermost nappe (Hangendserie) contains eclogites and paragneisses which were both affected by early Variscan high-pressure metamorphism. A dark, kyanite-free eclogite (Mg# ~45–70, Al₂O₃ ~13–16 wt.%) can be distinguished from a light, Ky-bearing eclogite (Mg# ~70–85, Al₂O₃ ~18–21 wt.%, usually higher Cr and lower HFSE contents, positive Eu/Eu*). Amphibolite facies metagabbros in the underlying nappe (Liegendserie) were commonly considered as potential lower-pressure equivalent of the light eclogites due to chemical similarities and similar late Cambrian/early Ordovician protolith ages. However, the interrelation and geodynamic interpretation of dark eclogites, light eclogites and metagabbros remained uncertain.

For many major and immobile trace elements (e.g., HFSE, REE), most of the dark and light eclogites form a continuous, linear array when plotted against Zr contents. Immobile-element discrimination diagrams classify them between E-MORB and N-MORB. Due to their high Th contents, the light eclogites are in an array with values of the dark eclogites and arc basalts. The metagabbros also show a moderate arc basalt component, but have more within-plate character than the eclogites due to high Nb/Yb, Nb/Zr and Ta/Hf ratios. Most eclogites have elevated δ¹⁸O values (+5 to +11‰) that correlate with Li, B, Bi and Sb contents. The metagabbros (δ¹⁸O ~+10‰) are similarly enriched in these elements.

Based on major and trace elements, the light eclogites are identified as plagioclase-rich cumulates, similar to the metagabbros. The dark eclogites behave as a chemical counterpart of the light eclogites and are thus likely derived from the same parental magma. A few samples have a more depleted signature, indicating either a different magmatic origin or a strong fluid-induced metasomatic overprint. Thorium enrichment in the light eclogites can be explained by crustal contamination, which also affected the metagabbros (see Stosch & Lugmair, 1990; Bosbach et al., 1991). But crustal contamination cannot explain the high Nb/Yb, Nb/Zr and Ta/Hf ratios of the metagabbros, the protoliths of which appear to be derived from a more enriched mantle source than those of the light eclogites. Nevertheless, for both units, crustal contamination indicates a continental rather than oceanic origin, and seafloor alteration is evident from δ¹⁸O correlation with Li, B and Sb. The Hangendserie and the Liegendserie therefore appear to be parautochthonous to each other, suggesting that the protoliths of the eclogites and metagabbros have formed within the same large-scale extensional tectonic setting in the peri-Gondwanan realm that accompanied the opening of the Rheic Ocean.

REFERENCES
Unravelling the tectono-metamorphic history of the Monte Rosa nappe: cirque du Véraz, upper Ayas valley, Italy

Joshua D. Vaughan-Hammon*, Cindy Luisier**, Lukas Baumgartner*, Stefan M. Schmalholz*

* Institute of Earth Sciences, University of Lausanne, Lausanne 1015, Switzerland (joshua.vaughan-hammon@unil.ch)
** University of Rennes, CNRS, Géosciences Rennes UMR 6118, Rennes, France

The Monte Rosa tectonic unit is a prominent nappe in the Western Alps, it consists of pre-Variscan paragneisses, intruded by Permian-age granitic bodies, later incorporated into the Alpine orogeny. The current position of the basement complex resides within the collisional Austroalpine-Penninic wedge, between the ophiolite units of the overriding Zermatt-Saas and the underlying Antrona. The basement complex derives originally from the upper crust of the pre-Alpine distal European passive margin, prior to Alpine continental collision. A spectacular area to observe the exposed Monte Rosa nappe complex as well as the overriding ophiolite units of the Zermatt-Saas is at the head of the Ayas valley branching from Aosta valley (northern Italy), in an area named “cirque du Véraz”. Recent glacial retreat has enabled detailed mapping, structural analysis and the collection of a wide range of lithologies in order to piece together the (poly-)tectono-metamorphic history of the Monte Rosa nappe. We will present the key findings of our investigations as well as newly documented outcrops.

As well as the lithological variability of the Monte Rosa basement exposed at the cirque du Véraz, continued attention has been focused here regarding its metamorphic variability, specifically during peak Alpine metamorphism, namely in pressure. The ongoing discussion concerning metamorphically-recorded pressure variations in the Monte Rosa nappe has been prompted by a wide range of peak metamorphic conditions calculated; with pressure estimates ranging between 1.2 and 2.7 GPa and temperature estimates between 490 and 640 °C. The highest pressure eclogite conditions recorded for the Monte Rosa nappe primarily involve minor volumes of unique assemblages termed ‘whiteschists’ at 2.2 GPa (chloritoid, talc, phengite, quartz ± kyanite/garnet). The cirque du Véraz field area, contains the largest concentrations of these unique high pressure mineral assemblages compared to anywhere else in the Monte Rosa nappe. Recent work, has highlighted large disparities in peak Alpine pressure between whiteschist (2.2 GPa) and metagranite (1.4 GPa) assemblages, as well as between whiteschist (2.2 GPa) and metapelitic (1.6 ± 0.2 GPa) assemblages, resulting in a P difference of 0.6 ± 0.2 GPa for the same metamorphic event (peak Alpine orogenesis). We present detailed petrological investigations and pseudo-section modelling of a newly exposed whiteschist body at the cirque du Véraz area.

Two whiteschist samples have been investigated with variable grainsize. A fine grained sample consist of perfectly preserved assemblage of <1mm sized chloritoid, as well as phengite + talc + quartz. These assemblages reveal peak metamorphic conditions (with a Mg-talc activity correction) at 2.1 GPa and 560 ± 10 °C, for Alpine orogenesis. This sample also displays a schistosity that coincides with a ductile deformation event that closely post-dates peak Alpine metamorphic conditions associated with a top-N shear sense related to nappe emplacement. A second whiteschist sample contains a similar peak paragenesis but with coarse grained >1cm sized chloritoid, as well as phengite + talc + quartz. Chlorite is also observed in this sample reflecting minor retrogression, with metamorphic conditions (with a Mg-talc activity correction) at 1.95 GPa and 560 ± 20 °C. Coarse grained chloritoids show significant zoning in Mg and Fe, with low XMg (~0.32) in the cores, increasing to high XMg values at the rims (~0.57). We interpret these zoning patterns to represent chloritoid growth during prograde Alpine metamorphism to eclogite conditions. We compare thermodynamically predicted Mg content of chloritoid for a range of prograde pathways, with measured Mg zoning from natural samples.
P 2.13

Triple oxygen isotope trend recorded by Precambrian cherts: A perspective from combined bulk and in situ secondary ion probe measurements

David Zakharov*, Johanna Marin-Carbonne*, Julien Alleon* & Ilya Bindeman**

*Institute of Earth Sciences, University of Lausanne, CH-1015 Lausanne (david.zakharov@unil.ch)
**Department of Earth Sciences, University of Oregon, Eugene, Oregon, 97405 USA

There are large uncertainties associated with the current estimates of temperature and oxygen isotope composition of Precambrian oceans, largely due to preservation issues inherited by the sedimentary record. The advancing ability to measure triple oxygen isotope ratios at the precision of 0.01 ‰ or better provides an opportunity to distinguish between signals captured during deposition, early diagenesis and late alteration of marine sediments. Here we undertake a triple oxygen isotopic study of marine cherts that formed at 3.5 and 1.9 Ga using a suite of samples from the Dresser (Australia), Kromberg, Mendon (S. Africa) and Gunflint (Canada) Formations. To disentangle the effects of recrystallization on a case-by-case basis, we combined: i) triple oxygen isotope measurements by bulk laser fluorination; ii) in situ secondary ion probe (SIMS) measurements; iii) Raman spectroscopy of organic matter. Within the studied samples the δ30Si and δ18O values measured by SIMS span over several ‰ at the scale of 10-100 µm, informing us of mixing arrays that are expected in the triple oxygen isotope space. To draw parallels with the envisioned environments for Archean silica deposition, we use geothermal amorphous silica scale that precipitated at ~188 °C as a result of high temperature seawater-basalt reaction at Reykjanes system in Iceland. The triple oxygen isotope signature of our Archean samples with negative δ30Si values is consistent with precipitation of microquartz at 150-170 °C. We suggest that at least some Archean cherts formed in equilibrium with fluids that are 1-2 ‰ higher in δ18O and ~20-30 per meg lower in Δ17O0.528 than the contemporaneous seawater due to the influence of submarine vent fluids. The 1.9 Ga Gunflint chert contains high-δ18O generation of microquartz (+24-26 ‰) that likely reflects early crystallization from marine siliceous sediment, which we assess using trace element concentrations and silicon isotope measurements. The δ18O – Δ17O of such quartz are consistent with the temperature of 60-80 °C, given that the pore water fluids had δ18O of around -2 ‰. The extrapolation of vent fluids and marine pore water fluids towards pristine seawater does not require a hydrosphere with δ18O outside of ± 2 ‰ of modern value. Instead, we propose that Archean cherts, at least partially, reflect mixing between marine and hydrothermal sources of silica, while the Paleoproterozoic Gunflint formation reflects maturation of siliceous sediment in presence of marine pore fluids.