

$^{40}\text{Ar}/^{39}\text{Ar}$ age constraints for the D2 Variscan extension in the Porto-Viseu metamorphic belt (Portugal)

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The Porto-Viseu belt is located in the innermost zone of the Iberian Variscan Belt. During the Variscan continent – continent collision (370-290 Ma), this area was affected by three main deformation events (D1, D2 and D3). The earlier D1 deformation phase affected all the pre-Carboniferous sedimentary sequences and induced prograde metamorphism of Barrovian type, characterized by a rapid increase of metamorphic grade from the chlorite and biotite zones to the staurolite, sillimanite and sillimanite+K-feldspar zones.

The D1 NW-SE trending contractional structures were variably overprinted by a major syn-collisional D2 extensional event attributed to a gravitational collapse of the thickened continental crust. The metamorphic climax, accompanied by intense migmatization is reached during this tectonic event. Late stage D3 deformation is related to crustal-scale transcurrent shear zones and marks the beginning of extensive plutonic activity represented by large volumes of syn- and late-D3 granitoids.

This work presents new geochronological $^{40}\text{Ar}/^{39}\text{Ar}$ data for D2. The data were obtained in muscovite concentrates from one metapelite sample (144-186) from the staurolite zone showing a strong S2 fabric. The muscovite concentrates yield a $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age of 333.3 ± 2.2 Ma (Figure 1). This age is coherent with regional structural constraints and with the available U-Pb geochronological data for the syn-D3 granites from the area (308 Ma). The 333.3 ± 2.2 Ma age appears therefore to date the D2 event.

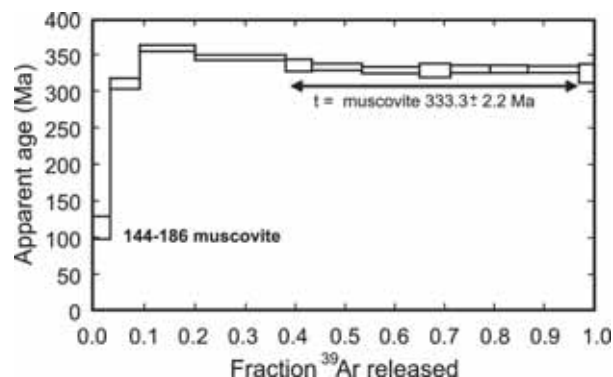


Figure 1: Muscovite $^{40}\text{Ar}/^{39}\text{Ar}$ analytical results.

This work was financially supported by the project CHRONOTECT-POCTI/CTE-GIN/60043/2004.

Imagery-correlated high precision stable isotope analysis

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The CAMECA IMS-1280 large radius, multicollector ion microprobe at the Wisc-SIMS National Facility is capable of high accuracy and precision for *in situ* analysis of isotope ratios. Spot size is variable from ~10 to sub-micron as dictated by counting statistics and desired precision, which can be as good as $\pm 0.1\%$ (1sd) for 10 μm spots and better than $\pm 1\%$ for sub- μm spots on $\delta^{18}\text{O}$ [1]. Analysis is correlated to textures as seen by a range of imaging techniques. These new capabilities permit exciting and fundamental research where samples are small, precious, or zoned. For instance:

1. Laser confocal microscopy reveals annual layers in speleothems from Soreq Cave, Israel. Correlated analysis of $\delta^{18}\text{O}$ detects long term changes in seasonality at 0.1y resolution, vs. >10y by previous methods [2].
2. Igneous zircons with 1-70 ppm Li have growth zoning, imaged by CL and by maps of ppm [Li]. Values of $\delta^7\text{Li}$ (and total REE) correlate to growth bands demonstrating that values are magmatic [3].
3. Growth zones in single forams (SEM) analyzed for $\delta^{18}\text{O}$ with <3 μm spots reveals up to 3‰ zoning between ontogenetic and gametogenetic calcite demonstrating two vital effect mechanisms that are opposite in sign [4].
4. Carbonate globules in the Mars meteorite, ALH84001, are concentrically zoned in Ca-Mg-Fe-Mn (EMPA). Values of $\delta^{18}\text{O}$ correlate with chemistry, while $\Delta^{17}\text{O}$ is constant at 0.8 for carbonates and 0.3 ± 0.1 for opx [5].
5. In chondrules from Semarkona, $\delta^{18}\text{O}$ vs. $\delta^{17}\text{O}$ slopes of ~0.5 are resolved within apparently MIF arrays [6].
6. CL imaging of quartz overgrowths in St. Peter sandstone (SW Wisconsin) reveals multiple layers of finely banded cement. However, analysis of $\delta^{18}\text{O}$ shows that cements are homogeneous at 29.3‰ suggesting that these syntaxial overgrowths formed in the vadose zone as deep silcretes [7].
7. Analysis of 2mm bluegill otoliths resolves seasonal changes of $\delta^{13}\text{C}$ in daily growth layers (SEM). A sharp $\delta^{13}\text{C}$ increase of ~10‰ during a whole-lake ^{13}C labelling experiment shows that a larger proportion of otolith carbon is derived from DIC than diet (M~0.4) [8].

[1] Page *et al.* (2007) *Am Min* **92**, 1772-1775. [2] Orland *et al.* (2008) *GCA*, this vol. [3] Ushikubo *et al.* (2008) *GCA*, this vol. [4] Kozdon *et al.* (2008) *GCA*, this vol. [5] Valley *et al.* (2007) *Lun Sci Conf* **38**, #1147. [6] Kita *et al.* (2007) *Lun Sci Conf* **38**, #1791. [7] Kelly *et al.* (2007) *GCA* **71**, 3812-3832. [8] Weidel *et al.* (2007) *Can J Fish Aquat Sci* **64**, 1641-1645.

KindisP modelisation of the chemical stability of Zn-bearing phases in pyrometallurgical slags

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Materials collected from three Zn-industrial former sites contain various Zn-phases such as analogues to zincite (ZnO), franklinite (ZnFe₂O₄), hardystonite (ZnCa₂Si₂O₇), willemite (Zn₂SiO₄), petedunnite (CaZnSi₂O₆) and wurtzite (ZnS). These phases were formed during high temperature processes and are metastable under ambient conditions. They were affected by weathering and Zn neoformed phases are mainly hemimorphite (Zn₄Si₂O₇(OH)₂.H₂O), smithsonite (ZnCO₃) and goslarite (ZnSO₄.7H₂O).

Hemimorphite is typically developed on willemite, goslarite on zincite and smithsonite on zincite and hardystonite.

However, formation of secondary products widely depends on *in situ* chemical factors (pCO₂, pO₂, Eh, pH) and activities of associated ions (SO₄⁻, Ca⁺⁺...). Formation of Zn-carbonates and Zn-sulfates are then limited by calcite and gypsum precipitation.

Observations and models developed by KindisP, for which the database was updated with estimated free Gibbs enthalpies values, permit to describe this competition, to precise the fields of stability of primary and secondary phases as well as the role of external fluids. Dissolution of primary phases is most effective in acidic conditions, favored by sulfides dissolution. Neof ormation is highly dependent to the released elements.

In order to validate kinetics models, 1 year leaching experiments were carried out on polished sections in adjusted pH solutions (water, lime and citric acid). Materials are unstable in acidic conditions and equilibrium is reached with a pH increase.

Under weathering conditions, sulfides react first due to oxidizing conditions. Dissolution of melilites and willemite is underlined by an important release of Ca, Zn and silica, necessary to the precipitation of sulfates, carbonates and hemimorphite.

Modeling carbon and chlorine stable isotope fractionation to assess and quantify degradation of chlorinated ethenes in groundwater

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Degradation of chlorinated ethenes primarily occurs via reductive dechlorination in the anoxic core of pollution plumes, while lower chlorinated ethenes may additionally become oxidized at the more oxidized fringes of plumes. Assessing the occurrence of oxidation processes is complicated as reaction products (Cl- and CO₂) are usually already present in high background concentrations in groundwater. Compound-specific stable isotope analysis (CSIA) provides essential information as it enables to quantify the extent of degradation of an organic pollutant based on its observed change in isotopic ratio away from source zones. Furthermore, two-dimensional carbon and chlorine isotope analysis may enable discrimination among these two main degradation processes resulting in reliable degradation estimates if degradation is being shared over two competing pathways [1].

Carbon isotope fractionation during sequential reductive dechlorination of perchloroethene to ethene was simulated before [2]. This model has been integrated in a 3-D reactive transport model [3] to enable simulation of competing core- and fringe processes within pollution plumes, and extended to include chlorine isotope fractionation. Interpretation and simulation of chlorine isotope fractionation is different and less straightforward than carbon isotope fractionation because of (i) the high natural abundance of the heavy Cl-37 isotope resulting in various relevant isotopologues of each higher chlorinated ethene, and (ii) the removal of one chlorine atom during each sequential degradation step. First simulation results showed that chlorine isotope ratio patterns were strikingly different from carbon isotope patterns.

The model is being applied to simulate lab and field observations, while results of scenario modeling give insight in the spatial carbon and chlorine isotope ratio distributions of chlorinated ethenes that can be expected to occur at typical contaminated sites.

[1] Van Breukelen (2007) *Environ. Sci. Technol.* **41**, 4004-4010. [2] Van Breukelen *et al.* (2005) *Environ. Sci. Technol.* **39**, 4189-4197. [3] Van Breukelen & Prommer *Environ. Sci. Technol.* **42**, 2457-2463.

Fate and transport in environmental systems: Integrating experiments, theory and reactive transport modeling

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Reactive transport modelling is a powerful, yet underutilized, tool in subsurface contaminant remediation science. Reactive transport models can be used to represent, analyze and, ultimately, predict the chemical reactivity and ecosystem functioning of subsurface environments. Therefore, they provide a means to assess to what extent biodegradation, abiotic reactions and physical transport processes determine the spatio-temporal distributions of contaminants and their degradation products. To build these models, mathematical expressions for the rates of the biogeochemical transformation processes that affect the distributions of relevant chemical constituents and microbial biomasses are needed. Here, an integrated, three-step approach is presented. (1) Kinetic experiments with simplified model systems are designed to identify possible reaction pathways, formulate rate expressions and obtain expected parameter ranges. (2) *In situ* potential rates and parameter values are constrained by kinetic experiments performed directly with natural sediment, soil or aquifer material. (3) Reactive transport modeling is used to verify the proposed rate expressions and to perform sensitivity tests. Once calibrated, reactive transport models can help explore biogeochemical activity in subsurface systems where many microbial, chemical and physical processes are coupled to one another. Various biogeochemical processes are used to illustrate the integrated approach, with an emphasis on processes that either control or depend on the local redox conditions. The strength of reactive transport modeling is further demonstrated for cases where slow microbial growth hinders a realistic simulation of the corresponding microbial processes in the laboratory.

Quaternary weathering rates and marine geochemical budgets

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Modern riverine chemistry and discharge is commonly used to estimate the long-term flux to the oceans of the many chemical and isotopic species that have their primary source in the continental crust. Here we suggest that measurements of many modern rivers, only a few thousand years after a glacial period, are not representative of the long-term flux and we quantitatively assess the implications of such a suggestion for key marine geochemical budgets.

The last deglaciation saw a profound change in the weathering regime in many parts of the planet - from intense physical grinding on a relatively cold, dry Earth to stronger chemical weathering on a warmer, wetter Earth. Experimental studies show that the fresh sediments produced in the glacial period would have undergone a pulse of rapid chemical weathering during the early post-glacial period. Moreover, these same experimental studies have also shown that both radiogenic and stable isotopes in this early chemical weathering pulse would match neither the bulk rock/soil composition nor the long-term weathering flux. Finally, the time constant of the pulse implies that today's rivers still record more rapid weathering, and an unusual isotopic composition, than the long-term equivalents. The implication is that the material supplied by modern rivers to the oceans is not representative of the long-term flux.

These findings have major implications for long-standing problems in ocean chemistry. For example, while there is growing convergence between ocean floor hydrothermal fluid flux estimates based on independent tracer exchanges and simple thermal calculations, estimates based upon the oceanic ⁸⁷Sr or Mg balances that rely on the quantification of the modern riverine flux are more than an order of magnitude greater. For elements such as Sr and Mg, with long oceanic residence times, modern riverine measured fluxes do not provide appropriate estimates of the long-term inputs. These ideas are relevant to many elements, and their isotope systems, with residence times in the oceans that are longer than the time period since the last deglaciation.

Sedimentary provenance evidence for the origin of the Gamburtsev Subglacial Mountains, Antarctica

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The Gamburtsev Subglacial Mountains are one of Earth's most enigmatic mountain ranges. They are situated in the middle of East Antarctica and are buried under ~600 m of ice. They reach an elevation of more than 3000 m and a size which is believed to be similar to the European Alps. These dimensions give rise to extensive speculation about their origin and composition.

Here we present an indirect geochemical approach to the origin of the Gamburtsev Mountains, using sedimentary provenance tools. The inferred ancient river drainage pattern of East Antarctica suggest that sediments shed from the Gamburtsev Subglacial Mountains should be deposited within the Lambert graben and Prydz Bay. The sediments sampled come from fluvio-deltaic sand deposits at ODP Site 1166 in Prydz Bay, predating the onset of East Antarctic glaciation.

Bulk sediment Sm-Nd model ages indicate an average crust formation age for the sediments' sources of ~2.0 Ga. Results for U-Pb dating of detrital zircons, reveal a significant age population of ~530 Ma, which is accompanied by a ⁴⁰Ar/³⁹Ar age population of ~519 Ma for detrital hornblendes. The similar ages of the dominant peak, suggest a rapid cooling from a major orogenic event at about 530 Ma. We see no evidence of significant young crustal contributions to the sediments that would be expected if the Gamburtsev Subglacial Mountains were of volcanic origin. The results point to a Pan-African origin of the mountains, and leave as enigmatic their great height and size.

In situ silicon isotope analysis of cherts by laser ablation MC-ICPMS

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We present *in situ* stable Si isotope measurements on four Archean Cherts from the Pilbara region, Western Australia. In this study we used a Microlas Geolas laser ablation (LA) system equipped with a 193 nm Excimer laser that was connected to a ThermoFinnigan Neptune MC-ICPMS. Molecular isobaric interferences of ¹²C¹⁶O⁺, ¹⁴N₂⁺, ¹⁴N¹⁶O⁺, that are present on masses ²⁸Si, ²⁹Si and ³⁰Si, were resolved with the aid of a medium resolution slit (RP=4000). An ablation pit size of 49 by 300 μm with a 7 Hz repetition rate and 5 J.cm⁻² was used. The LA measurements on the MC-ICPMS were made with the same setup as described by [1]. To access precision, accuracy and matrix effects of the LA technique, chert samples were analyzed that were previously characterized for silicon isotopes by micro-drilling and subsequent liquid chromatographic purification [2]. A chemically homogenous chert sample that is well characterized for silicon isotopes by wet chemical techniques and has a δ³⁰Si of 0.50±0.20 (2 sd, n=4, relative to NIST RM8546) was used as a standard.

Matrix effects were evaluated by mixing the particle flow from the laser with the output from a desolvating nebulizer, in which elemental standard solutions of the major elements were aspirated. The signal intensity of the major elements from the dissolving nebuliser was varied from 25% to 100% of the ²⁸Si signal produced by laser ablation. Significant shifts (more than 2 ‰ in the δ³⁰Si) were found for the elements Ca and Al. Therefore, the use of a standard with a similar composition as the samples is mandatory for this laser ablation method. We obtained a precision of better than 0.26 (2 sd), which is slightly better than the 0.30 for solution work [1]. Micro-drill and laser data are in excellent agreement (differences of less than 0.4 ‰). This new laser ablation technique therefore opens new possibilities to unravel the depositional mechanisms for Archean cherts.

[1] Van den Boorn *et al.* (2006) *J. Anal. At. Spectrom.* **21**, 734–742. [2] Van den Boorn *et al.* (2007) *Geology* **35**, 939–942.

Reconstructing fluid chemistry from mineral-fluid partitioning using the lattice-strain model

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Fluids exert a key control on processes in the Earth, from plate tectonics to ore formation. In order to understand and model these processes, it is therefore essential to know the properties of the associated fluids. Such information can be derived from the chemistry of the fluids, which also provides clues about the nature of the host environment. Unfortunately, it is rarely possible to determine the composition of these fluids directly and in most cases this must be reconstructed from the mineralogical and metasomatic imprint of the fluid on its host rock. However, at present such reconstructions are largely limited to the major constituents of the fluid, whereas it is the trace constituents, which are generally the most indicative of processes and host environment.

Lattice-strain modeling of mineral-fluid partitioning offers a potentially powerful means for quantitatively evaluating fluid composition. When the partitioning of elements between fluids and minerals is known at representative conditions, the chemistry of a fluid can be reconstructed from the composition of coexisting minerals. This approach is particularly suited to reconstructing the trace element composition of fluids. Furthermore, it allows the evolution in fluid chemistry to be determined from minerals formed at progressively later stages in the paragenesis. We present here the results of well-constrained mineral-fluid partitioning experiments and use the systematic behaviour in partitioning, as described by the lattice-strain model, to interpolate and extrapolate these data to conditions and elements outside those of our experimental system.

Previous application of lattice-strain modeling to mineral-fluid partitioning has been ambiguous. Our experiments indicate that this is due to non-uniform element speciation in the fluid. When such effects are accounted for, or where speciation is uniform, the lattice-strain model provides an excellent description of mineral-fluid partitioning. Given the ubiquity of fluids in the Earth and their control on a range of processes, this approach will provide a valuable and widely applicable tool.

Fluid flow rates and sediment pore-fluid interactions at the Carlos Ribeiro mud volcano (Gulf of Cadiz)

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Extensive research over the last eight years in the Gulf of Cadiz (NE Atlantic) has revealed a large number of hydrocarbon-related fluid flow structures including more than 25 mud volcanoes (MVs). A high resolution geochemical data set was collected from the Carlos Ribeiro mud volcano (2200m; deep Portuguese margin) to study sediment pore-fluid interactions in MVs. Quantification of fluid flow rates and composition is valuable as MVs function as an important element source for deep-water ecosystems in these environments. Piston, gravity and mega cores were recovered from five sites located on a 380 m long transect from the apex of the MV to mudflow pathways southeast of the crater. Extracted pore-waters show a strong and continuous depletion in chloride (Cl) content with minimum values of 200 mM at the centre of the MV crater, suggesting a freshwater source from below. Major cation concentrations indicate clay mineral dehydration as a possible source of low salinity fluids. High total alkalinity and hydrogen sulfide concentrations are present in the near surface sediment which is commonly related to a chemosynthetic ecosystem driven by the anaerobic oxidation of methane. Smear slide observations revealed the presence of secondary processes such as dolomite and pyrite formation altering pore-water and sediment chemistry. Clay mineral data on mud breccia and clasts will be used to assess sources and diagenetic reactions within the Carlos Ribeiro MV. Applying a 1-D transport-reaction model to conservative pore-water constituents (chloride and boron), we estimate an upward fluid flow rate ranging from 14 cm yr⁻¹ in the centre of the crater to 2 cm yr⁻¹ on the periphery. The upper range of these fluid fluxes from Carlos Ribeiro MV is higher than most Gulf of Cadiz MVs, and similar to values estimated for Captain Arutyunov MV, identified as the most active MV in this area so far [1, 2].

[1] Hensen *et al.* (2007) *Geochim. Cosmochim. Acta* **71**, 1232-1248. [2] Niemen *et al.* (2006) *Geochim. Cosmochim. Acta* **70**, 5336-5355.

Constraining rates of crustal recycling using geophysical and geochemical methods

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Whatever its origin the continental crust has been maintained by growth via arc magmatism during the Phanerozoic [1]. This gain is balanced by large volumes of continental crust that are reworked back into the upper mantle via subduction zones. Whether a particular margin is in long-term accretion or is the location of net tectonic erosion crustal materials are delivered to depth beneath the arcs via the subduction channel, which is fed by material removed from both the toe of the forearc and its under surface [2]. Globally we estimate that around 3 Armstrong Units (1 AU = 1 km³/yr) are subducted to depth, of which 1.65 AU comprises subducted sediments and 1.33 AU tectonically eroded forearc crust. Estimates of crustal subduction by the loss of passive margin crust during continental collision events indicate around rates of 0.4 AU for the Cenozoic, suggesting this is not the dominant process in crustal recycling. Geochemical data can be used to estimate how much of the subducted sediment is returned to the crust via arc magmatism. Rates vary widely between arcs, with as much as 80% recycling in Costa Rica, but <5% for the Kamchatka and Lesser Antilles Arcs. Globally around 23% of the subducted material is reworked into arc magmatism. The remaining 77% is subducted deeper in the upper mantle. Erosional flux from the continents to the trenches is the primary control on margin tectonic character [3] and in turn this is linked to climate. Faster erosion during glacial-interglacial cycles means that the margins are more accretionary at the present time than is typical in the past. Erosion is generally able to remove excess crustal thicknesses generated by orogeny within 200 m.y. As such it is the key control on crustal thicknesses and is itself governed by sealevel and the volume of water in the global ocean.

[1] Rudnick (1995) *Nature* **378**, 573–578. [2] Vannucchi *et al.* (2008) *Nature* **451**, 699–704. [3] Clift & Vannucchi (2004) *Rev. Geophys.* **42**, RG2001.

⁴⁰Ar/³⁹Ar dating in Thor-Odin dome, British Columbia, Canada: Excess Ar in high-grade migmatitic rocks

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⁴⁰Ar/³⁹Ar hornblende and biotite dating was carried out in the core of the southern Canadian Cordillera to investigate the significance and behaviour of excess argon in migmatites, and to place constraints on tectonic models. High-grade rocks of the Thor-Odin dome, in the Monashee Mountains, were deformed and underwent anatexis at mid-crustal levels during Late Cretaceous to Eocene orogenesis ([1] and references therein). The cause of Eocene denudation is controversial (e.g. extension, extrusion or diapirism). ⁴⁰Ar/³⁹Ar samples from an ~12 km thick structural section of cord-sil-kf-melt, sil-kf-melt and sil-st grade rocks coincide with U-Pb geochronology sample sites.

As is the case in Thor-Odin dome, ⁴⁰Ar/³⁹Ar cooling dates from migmatitic rocks may be unreliable indicators of cooling history because excess argon may cause cooling dates to be significantly older than is geologically reasonable. In the sampling transect, hornblende yields ⁴⁰Ar/³⁹Ar plateau ages ranging from 88 to 52 Ma. In most samples, the release spectra show components of excess argon. There is an apparent correlation between increasing hornblende dates, an increasing component of excess argon and structural position of the samples, and the Late Cretaceous dates in the core of the dome are “too old” relative to the ca. 56–54 Ma timing of anatexis based on U-Pb geochronology studies from the same rocks [1]. Excess argon may have originated within basement rocks and may be a consequence of short residence time of the rocks at high temperatures; this is under investigation. In contrast to the hornblende data set, the biotite cooling dates show little variation with respect to structural level, and their release spectra show no observable excess argon.

Interpretation of robust ⁴⁰Ar/³⁹Ar data, in conjunction with other data sets and geological observations, do not support detachment faulting on the southwest flank of the dome and support models whereby the domal geometry had formed prior to exhumation on bounding extensional fault systems.

[1] Hinchey *et al.* (2006) *Can. J. Earth Sci.* **43**, 1341–1365.

Towards computer simulation of element complexation in subduction zone fluids

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Field-based evidence as well as laboratory experiments suggest rare earth elements (REE) can form chloride, fluoride, hydroxide and sulphate complexes in hydrothermal fluids. In addition to effects of pressure and temperature, the presence and concentrations of these ligands are thus likely to play a critical role in determining REE mobility in subduction zones. But to date, the atomic-scale processes controlling elemental solubilities are poorly understood.

Pending accompanying high-pressure, high temperature mineral-fluid trace element partitioning experiments, we are investigating the configurations and energetics of REE complexes dissolved in H₂O at elevated pressures and temperatures using electronic structure theory.

A thermodynamic cycle was developed to obtain relative hydration free energies of REE ions using density functional theory. The first solvation shell is explicitly defined and the remaining part of the solvent is modelled using a polarisable continuum model, which can be augmented to mimic a broad pressure and temperature range.

Calculated relative hydration free energies for trivalent REE ions with eight- and nine-fold coordinated explicit first hydration shells show good agreement with experimental literature values at room pressure and temperature. The hydration free energy is more negative for smaller complexes (heavy REE) relative to larger complexes (light REE). We explore the energetics and geometries of lesser charged and neutral REE-anion complexes dissolved in H₂O. Preliminary results show enhanced REE complexation in the presence of anions.

With increasing temperature and pressure, the difference in hydration energies between HREE and LREE ions increases. If this were to dominate the thermodynamics, smaller complexes (HREE) would remain in solution in preference to larger complexes (LREE). This seems counter-intuitive given the observed high LREE/HREE ratios observed in island arc volcanics. Co-existing solids, either bulk or surface, must play a dominating role in controlling REE signatures.

Laser microprobe depth profiling of ⁴He diffusion in Durango Apatite

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To further demonstrate the utility of laser ablation methodologies in (U-Th)/He thermo- and geochronology [1] an artificial diffusion profile of ⁴He in Durango apatite has been studied by depth profiling.

A >200µm thick slab, cut from a larger apatite crystal, was polished and then heated under vacuum in a diffusion cell [2] at 400°C for 45 minutes. The slab was put in the laser chamber of the noble gas extraction line, and using a 193nm Excimer laser the sample was ablated with a 100µm spot size in 6µm depth increments. After gas purification and cryogenic separation, the ⁴He was analyzed by ion counting on a GVI Helix SFT mass spectrometer.

Fig. 1 shows that the experimental results match well with the calculated model loss curve based on experimentally derived bulk diffusion coefficients [3]. This result supports the experimental results of Farley [3] and demonstrates convincingly that laser ablation also provides an opportunity to resolve natural ⁴He diffusion and α-ejection profiles directly.

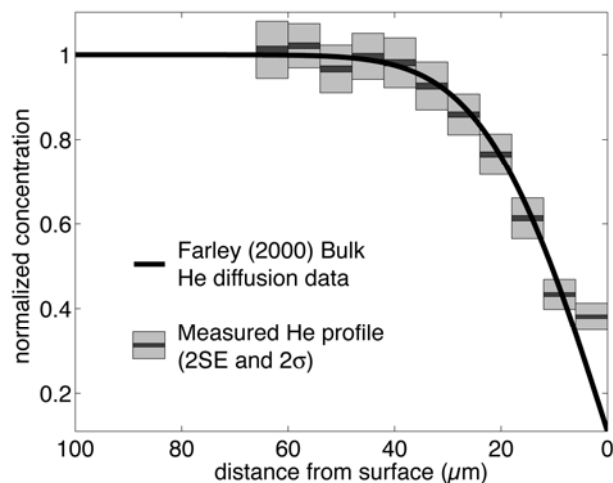


Figure 1: The measured ⁴He diffusion profile compared to the calculated apatite model loss curve.

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Underneath the magma ocean: Element distribution between calcium silicate perovskite and Sulphur- bearing iron melts

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Many attempts have been made to use the partitioning behaviour of elements in molten metal – *molten* silicate systems to constrain the conditions at which Earth's core and mantle last equilibrated during initial differentiation. It is now becoming increasingly obvious that observed mantle siderophile element abundances are not consistent with either single-stage or multiple stage metal-silicate melt equilibration at the bottom of a global magma ocean. Alternative hypotheses, such as heterogeneous accretion or mantle self-oxidation are being considered.

Missing from the current debate is an assessment of the role of partitioning between metal melts and *solid* silicate minerals in the lower mantle. At least some of the later stages of core formation must be characterized by liquid iron alloys in direct contact with a solid lower mantle matrix in the absence of silicate melt. In addition, the present-day core-mantle boundary is a region where molten core metal continues to be in contact with lower mantle minerals. Solid silicates have been in contact with core-forming metals for prolonged periods, leading to partial equilibration at a minimum.

We experimentally determined the distribution of a range of lithophile and siderophile elements between calcium silicate perovskite (CaPv) and molten sulphur-bearing Fe at pressures of 23-24 GPa and temperatures in the range 1623-1873 K. Chemical equilibrium was reached in our experiments despite low lattice diffusion rates in CaPv, probably through enhanced atomic mobility during phase transition of the wollastonite starting material. Our data show that in the presence of sulphur-rich liquids, Ni and Co behave significantly less siderophile in equilibrium with CaPv than if the same metal equilibrates with fully molten peridotite at the same depth and fO₂ conditions. Our results add another layer of complexity to attempts to quantitatively constrain core formation models using Earth's mantle composition.

Chemical weathering of mafic rocks in boreal environment (NW Russia)

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Numerous works have emphasized the significant role of silicate weathering in atmospheric CO₂ consumption and climate regulation. However very few studies exist that estimate the impact of chemical weathering in environment underlain by mafic rocks such as gabbros and olivenite. In the Northwestern part of Russia, in the Karelia and Kola provinces belonging to the Eastern Fennoscandian Shield, coexist mafic (e.g., olivenite, gabbro-norite) and felsic (e.g., gneiss, granite) types rocks. These zones are characterized by the full-scale presence of quaternary deposits (e.g., moraine) of Pleistocene age. Soils are mainly podzolic and hydromorphic in the depression zones. The main part of the studied zone belongs to the boreal taiga forest ecosystem with pine, spruce, birch, ericaceous species and moss. The arctic climate is marked by a snow-free period of 4-5 month (june to september), a mean annual temperature close to 0°C, and a mean precipitation amount between 550 and 700mm/yr. Investigations were conducted on rocks (i.e., mafic and felsic), soil and water samples taken within the Kivakka and Vetreny Belt magmatic formations during extensive sampling campaigns. This work is based on majors and traces elements analysis (i.e., ICPAES, ICPMS, microprobe), Sr isotopic measurements (i.e., TIMS) and mineralogical investigations (i.e., XRD, MEB).

Mineralogical studies performed on soils samples show ubiquitous quartz or zircon whatever the nature of the parental rocks (i.e., mafic and felsic). Chemical analysis (e.g., major elements, Sr isotopes) put in evidence the strong influence of the morainic contribution to soils chemistry and mineralogy. In this context, calculations of weathering intensity based on bulk major and traces elements analysis are not suitable. Surprisingly, surface waters flooding felsic environment shows higher Ca/Na and Mg/Na molar ratios than water draining mafic rocks, while Sr isotopic signatures of water and soil samples are similar. The data suggest that Ca-Mg vermiculite formation in soils and mineral phases belonging to the moraine partly control major elements signatures in surface waters. This should be taken into account in the estimate of mafic rocks weathering rates and calculations of atmospheric CO₂ consumption by weathering in such particular environment.

Origin of “quartz eyes” and fluid inclusions in mineralized porphyries

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Formation of porphyry-style ore deposits starts with the metal extraction from magmas at so-called magmatic-hydrothermal transition (MHT). The processes and compositions at MHT are difficult to study as the record of them is poorly preserved. As the MHT is characterized by massive crystallization of quartz, including quartz “eyes” and veins, their study can elucidate questions related to metal transport and deposition. Quartz grains from the porphyry deposits all over the world (Antapaccay, Peru; Batu Hijao, Indonesia; Climax, USA; Panguna, PNG; Far Southeast porphyry, Philippines; Rio Blanco, Chile; Omsukchan, Russia) were studied by optical, SEM-CL and BSE microscopy, electron microprobe and LA ICPMS.

Quartz grains, even within each sample, have different shapes (rounded, egg-shaped, amoeboid or euhedral) and cathodoluminescence (CL) patterns (shape, number and width of bands in CL images). The outer layers of quartz are markedly different, which is unexpected if the grains had formed in the same conditions. The zones that are dark and bright in CL have different area proportions in grains occurring next to each other. The CL pattern is sometimes extremely irregular. CL layers in many cases mimic grain boundaries. According to microprobe and LA ICPMS data the CL intensity depends on the concentration of the impurities Al, Ti, Fe and Li. Different CL layers are different in structure - the brighter bands are more crystallographic and brighter grains are more euhedral. Inflections and blurring of CL bands are often structurally associated with fractures.

The data show that the quartz “eyes” could not crystallize from a silicate melt as normal phenocrysts. It is very likely that *in situ* segregation of residual SiO₂- and H₂O-rich liquid and its solidification followed by coagulation (e.g. formation of silica-gel globules) took place in the magma (crystal mush) during MHT. Such globules could remain in a plastic state for a long time even at rather low temperatures. The solidification of globules occurred after bands of different composition had formed and led to fracturing of solidified and inflection of unconsolidated layers. All fluids (liquid and vapour) released from the original silica-gel during solidification were trapped as inclusions (aqueous, salt-rich and sulphide).

Geochemical and microbial controls of the decomposition and dispersion of depleted Uranium in the environment: Experimental studies

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Depleted uranium (DU) is now commonly utilised in armour piercing munitions. The majority of DU entering the environment does so as large pieces of DU alloy. After impact, DU deposits on the ground and other surfaces, generally in the form of partly oxidised fragments. Penetrators which hit soft targets such as sand or soil can penetrate to depths of >50cm and stay intact for long periods. Largely intact penetrators may end up in the sea or in bodies of freshwater. The environmental fate of DU fragments is still not well known, and there are obvious concerns regarding potential contamination of soils or groundwaters.

Currently we are involved in a multidisciplinary study of laboratory model systems aimed at providing a predictive understanding of the processes involved in DU decomposition and dispersion. The role of bacteria and fungi in DU decomposition (and, in turn, the impact of DU on bacterial and fungal communities) in addition to (geo)chemical factors are being studied. Model systems representative of a considerable range of natural environments (loamy, sandy or cementitious soils, estuarine sediments of differing salinities) and specific conditions (aerobic, anaerobic, abiotic or with fungi or bacteria present) have been studied and shown to exhibit important differences in breakdown behaviour and hence uranium mobility. For example, under conditions representative of a loamy soil, anaerobes may inhibit DU corrosion whereas pitting corrosion occurs under biotic aerobic conditions. DU appears initially to corrode to U⁴⁺ oxide and subsequently form secondary U compounds via dissolution and reprecipitation.

Geo-microbial prospecting method for hydrocarbon exploration in Vengannapalli village, Cuddapah Basin, Andhra Pradesh, India

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Geo-microbial prospecting for hydrocarbons is an exploration method based on the seepage of light hydrocarbon gases and their utilization by hydrocarbon oxidizing bacteria. The detection of anomalous population of methane, ethane, and propane oxidizing bacteria in the surface soils or sediments, helps to evaluate the prospects for hydrocarbon exploration [1, 2]. This method has been applied in Vengannapalli village, Cuddapah Basin, as natural leakage of gas from boreholes was reported.

In the present study, the bacterial populations was found to be maximum of 5.4×10^5 cfu/gm, 5.5×10^5 cfu/gm and 4.6×10^4 cfu/gm of soil for methane, ethane and propane oxidizing bacteria respectively. The microbial results indicate the anomalous population of methane, ethane and significant propane oxidizing bacteria were found in survey area. The bacterial concentration distribution maps follow the same pattern and significant anomalies have been observed in the northeastern and southwestern parts of the studied area. The adsorbed soil gas analysis showed the presence of moderate to low concentration of methane (12.4 to 222.8 ppb), ethane (3 to 35.9 ppb), propane (2 to 24.3) and butane (18.4 ppb). The study reveals good correlation between adsorbed soil gas and microbial studies, overlaying of these anomalies indicate the natural model of 'Halo' pattern. The $\delta^{13}\text{C}_1$ analysis of most of the samples show enriched carbon isotopic data of methane ranging from -35.0 ‰ to -10.6 ‰ indicating methane derived from coal/ Type III kerogen. Based on the microbial, adsorbed soil gas and carbon isotope studies, presence of hydrocarbon micro-seepage has been referred the area to be worth visiting for conventional hydrocarbons.

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Effect of Mn(II) on the oxidative dissolution of biogenic UO_2

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Bioremediation of U(VI) contaminated sites is predicated on the stability and long-term immobilization of the bioremediation product: biogenic uraninite (UO_2). Preventing re-oxidation of UO_2 is an important aspect governing the success of bioremediation. The goal of the study was to evaluate the effect of divalent cations on the structure and reactivity of biogenic UO_2 . Thus, UO_2 was produced biologically in the presence of Mn(II), a divalent cation ubiquitous in the groundwater.

U(VI) reduction was carried out at two different pH values (6.3 and 8.0). The presence of 1mM or 5mM Mn(II) did not significantly affect U(VI) reduction. A method involving alkaline treatment followed by organic phase separation was developed to separate UO_2 from the biomass in order to perform spectroscopic and reactivity characterization. Characterization techniques included imaging with conventional TEM, BET determination of surface area, adsorption and dissolution experiments, and synchrotron-based analyses (XANES, EXAFS, WAXS spectroscopy).

Sorption experiments showed uptake of Mn(II) by UO_2 at near neutral and alkaline pH, but rule out significant sorption at and below pH 5. Thus, Mn(II) sorbed onto biogenic UO_2 during its synthesis was removed by multiple washes using water buffered with MES at pH 5 until no further Mn(II) could be desorbed. A mass balance study (involving acid digestion) and EXAFS measurements indicated that, prior to the pH 5 wash, the majority (~92%) of Mn(II) associated with UO_2 was adsorbed. However, after the wash, Mn(II) was found to be predominantly incorporated into the UO_2 crystal structure. To date, oxidative dissolution experiments using air as an oxidant indicate that the presence of Mn(II) does not significantly affect biogenic UO_2 dissolution rates at pH 6.3, but that at alkaline pH values, Mn(II) accelerates oxidative dissolution significantly.

Biospheric coupling of terrestrial water and carbon fluxes: Implications for the climate system

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Terrestrial water and carbon fluxes represent one of the largest movements of mass and energy in the Earth's outer spheres, yet the relative contributions of abiotic water vapour fluxes and those that are regulated solely by the physiology of plants remain poorly constrained. By interpreting differences in the oxygen-18 and deuterium content of precipitation and river water, it is possible to partition plant transpiration from the evaporative flux that occurs directly from soils, water bodies and plant surfaces. The methodology was applied to fifteen large watersheds in North America, South America, Africa, Australia, and New Guinea, and results show that approximately two thirds of the annual water flux from the water-limited ecosystems that are typical of higher-latitude regions can be attributed to plant transpiration. In contrast to water-limited watersheds, transpiration in high-rainfall, densely vegetated regions of the tropics represents a smaller proportion of precipitation and is relatively constant, defining a plateau in response to incident solar radiation. Estimates of water transpiration behave similar to net primary productivity, confirming that, in agreement with small-scale measurements, the terrestrial water and carbon cycles are inherently coupled via the biosphere, offering a conceptual perspective on the dynamics of energy exchange between terrestrial systems and the atmosphere, where the carbon cycle is essentially driven by solar energy via the water cycle intermediary.

Ferguson & Veizer (2007) *J. Geophys. Res. – Atm.* **112**, D24S06, doi,10.1029/2007JD00 8431

Tracking the biogeochemistry of an Ediacaran basin in SW-Gondwana by isotopes and biomarkers

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In an ongoing project we trace the biogeochemical changes in Neoproterozoic to Cambrian sediments of the Corumba Group (CG, SW-Brazil), the Arroyo del Soldado Group (ASG, Uruguay), and Sierras Bayas Group (SBG, Argentina), all of them from the Rio de la Plata Craton, SW-Gondwana, by an isotopic and molecular approach.

The $\delta^{13}\text{C}_{\text{carb}}$ values range from -5.7 to 5.7% VPDB, and display coeval excursions in CG and ASG coinciding with global curves. The lowest values recorded for cap dolostones of the CG (Bocaina Formation) are typical in cap carbonates worldwide. The $\delta^{13}\text{C}_{\text{ker}}$ values varying from -26.4 to -22.8% in CG samples and from -27.4 to -12% in ASG are most likely due to variations in the primary composition of the organic matter (i.e., variable contribution of bacteria) and/or in the productivity rate during deposition. The highest $\delta^{13}\text{C}_{\text{ker}}$ values in ASG samples reflect isotopically heavy carbon primary sources or a ^{13}C -enriched surface water during water column stratification. The $\delta^{15}\text{N}_{\text{ker}}$ range between -3.3 to 3.1% N_2 -Air, suggests primary contribution of molecular nitrogen fixers (cyanobacteria). Positive $\Delta^{13}\text{C}_{\text{carb-ker}}$ excursions, higher concentrations of redox sensitive elements (Mn, Fe and V), ΣREE and variations in the Ce anomaly can be explained by an enhanced primary productivity (increased $p\text{CO}_2$ or nutrients supply) and preservation of organic carbon favored by reducing conditions in bottom waters. The main resolvable compounds in the GC-MSD total ion chromatograms of the hydrocarbons saturated fraction are *n*-alkanes in the C_{12} - C_{30} range (maxima at C_{21}) for CG; C_{14} - C_{35} range (maxima at C_{26}) for ASG and C_{14} - C_{28} range (maxima at C_{25}) for SBG samples with no odd/even C-number predominance. The high amount of $\text{C}_{>18}$ *n*-alkanes confirm a marine planktonic input. The identified biomarkers include extended C_{29} - C_{34} hopanes, acyclic isoprenoids, branched alkanes (8-methyl heptadecane), alkybenzenes and traces of steranes. Gammacerane was identified in one sample. Biosynthesis of homohopanes is restricted to bacteria not strictly anaerobic, and steranes are derived from aerobic eukaryotes. The 8-methyl heptadecane is typically synthesized by cyanobacteria. The biomarker distribution reflects a mainly microbial ecosystem based on photosynthetic primary production, including chemotrophic bacteria.

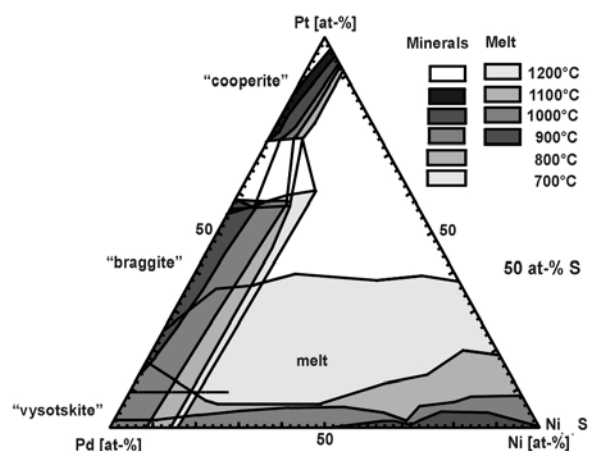
Phase relationships in the system PtS-PdS-NiS: Summary of previous results and new X-ray diffraction data

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Data and Sample Sources

Phase relationships in the dry system PtS-PdS-NiS (i.e. at metal:sulphur ratio of 1) at 700°C, 800°C, 900°C, 1000°C, 1100°C, and 1200°C have been shown by Verryin & Merkle [1] in an experimental investigation (Fig. 1). In natural examples as in the platinum-group element ores of the Bushveld Complex [2-5], of the Stillwater Complex [6, 7] and of Noril'sk [8], cooperite, braggite, and vysotskite display a distinct compositional variation in which the Pt/Pd ratio and the Ni content can vary significantly and will be shown.



Results

Comparative results of analytical techniques such as Raman spectroscopy, electron microprobe analysis as well as new X-ray diffraction data will be presented.

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Fluid-rock interaction in hydrothermal system at Kärdla impact structure, Estonia

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Meteorite impact induced hydrothermal (IHT) alteration is a specific type of hydrothermal process that has been recognized at numerous terrestrial impact craters varying in size and composition [1]. Kärdla impact structure (D=4km; 58°58'40"N, 22°46'45"E), one of the best-preserved and well-investigated impact structures of its size [2], serves as a type model for IHT activity [3,4] in small-to-medium sized complex impact craters at marine targets. The mineralogical, geochemical and stable isotope studies of the structure suggest three stages in the IHT evolution, characterized by different fluid-state conditions, temperature, alteration type and mineral phases [5].

Mineralogical characteristics of the IHT alteration in Kärdla correspond to the K-series during the initial stages, which then evolves into Ca-Mg-series in last stage of the cooling. Rapid precipitation of K-feldspar during the first stage suggests rather high pH (>8) of the circulating fluid. At the later stages the pH of the initial fluid was lowered, but remained high enough (>7) to promote the II type of K-feldspar and carbonate mineral precipitation. Due to interactions with aluminosilicate minerals the fluid became gradually enriched in respect to Ca-Mg. Precipitation of calcite/dolomite was controlled by the availability of Ca- and Mg-ions in the convecting fluids. The calcite I precipitated from a supersaturated solution, which resulted in an efficient removal of Ca, thus, allowing the precipitation of dolomite. Calcite II precipitation was initiated after removal of Mg by dolomite formation. At the final stage, precipitation of sulfides, Fe-oxyhydrates and calcite III occurred likely at temperatures close to the ambient conditions.

Compared to volcanic hydrotherms, IHT mineralization in Kärdla was apparently richer in dissolved oxygen, but not necessarily oxidative, and low in reduced compounds.

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A new perspective on the geochemical signature of Mt. Etna alkaline magmas

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The occurrence of LREE enrichment and HREE fractionation ($La_N/Yb_N = 18$) led many authors to hypothesize the presence of residual phases in the source of Etnean alkaline magmas that preferentially retain HREE, such as garnet. The occurrence of garnet was commonly bounded to lherzolites, thus implying the onset of partial melting at depth greater than 80 km. This would indicate the occurrence of a thermal regime related to an asthenospheric plume-like structure, whose evidence is still matter of debate. On the other hand, if such a structure does not occur, the melting process should be mainly under the control of slight pressure changes induced by regional lithospheric stretching at more shallow depth. Recent work has shown that partial melting of a source composed of both spinel lherzolite and garnet pyroxenite can produce sub-alkaline magmas, which can preserve a garnet signature at more shallow depth. Here, we investigate the role that partial melting of a heterogeneous metasomatized source, constituted of spinel lherzolite and garnet pyroxenite, can have in producing a trace element signature consistent with that observed for Etnean alkaline magmas. Xenoliths of deep provenance found in the Hyblean area indicate that silicate melts, and related metasomatic fluids, may have intruded a spinel lherzolite mantle to give origin to a garnet-bearing pyroxenite. As a result, the spinel lherzolite mantle is veined by garnet pyroxenite where phases related to metasomatizing agents, such as amphibole and phlogopite, have been stabilized. Mass balance calculations have been performed for simulating partial melting of such a source. Results have been compared with three representative mantle-equilibrated magmas, calculated by adding an ultramafic assemblage to compositions of the prehistoric lavas of Mt. Maletto, and of the 1763 and 2005 eruptions. Different proportions of spinel lherzolite and garnet pyroxenite, along with variable modal contents of metasomatic phases, can account for the trace element signature of the large spectrum of Etnean alkaline magmas and for their geochemical variability through time.

Xenolith evidence for anatexis of hydrothermally modified mafic crust (Hyblean area, Italy): Implications for primary origin of some trachytoid magmas

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Extensive fractional crystallization from primitive mafic magmas is one of the most common mechanisms to explain the origin of alkaline felsic volcanic rocks at ocean islands, often associated to the dominant basaltic ones. Nevertheless, this process fails to justify in some instances extreme basalt-trachyte bimodal magmatism and its odd volumetric relationships. Here, we focus on some hydrothermally-modified gabbroic xenoliths coming from the Hyblean Plateau (Southern Italy), which are considered to represent portions of a fossil, deeply altered, oceanic core-complex underlying the area. The hydrothermal mineral assemblage consists of Na-rich alkali feldspar, clay minerals (C/S interlayers), zeolites, aegirine-augite, titanite and rare hydrothermal zircon. Perfectly isotropic and clear glass blebs, which derive from xenoliths partial melting, make also peculiar the texture. Glasses exhibit perlitic microfracture sets and a lot of fluid inclusions having, sometimes, KCl daughter mineral. On the whole, the chemical composition of such a metasomatic rock shows higher contents in alkalis, Zr, Hf, U, Th, volatiles and lower CaO, MgO, FeO with respect to the pristine tholeiite gabbro.

The new dataset of major (EMPA) and trace elements (SIMS) has been obtained on the above-mentioned glass patches. Compositions display a mildly peralkaline character, with FeO_{tot}/Al_2O_3 ratios clustering at the boundary between the pantelleritic trachyte and comenditic trachyte fields. Na_2O/K_2O ratio is about 2.2, chlorine varies from 800 to 2500 ppm and fluorine is about 550 ppm. Trace element distribution is consistent with other natural trachytoid magmas, as evidenced by the comparison with trachytes from the neighboring occurrences of Pantelleria and Etna, and from various oceanic islands (i.e. Socorro Island, Ascension, Hawaii, Kerguelen, French Polynesia). Since high halogen fugacity dramatically decreases the melting point of various rock-forming minerals, anatexis of altered oceanic crust may be accounted for the origin of some trachytoid magmas.

Barroso-Alvão and Fregeneda-Almendra Pegmatitic Fields (Portugal and Spain): Mineralogical and geochemical comparison

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The Barroso-Alvão (BA) and Fregeneda-Almendra (FA) regions are known by their LCT (Li, Cs, Ta) pegmatites. Both pegmatite fields are located in the Iberian Massif (NW Iberian Peninsula). They are hosted in low- to medium-grade metamorphic rocks and surrounded by highly evolved synorogenic two-mica granitoids of the same age and geochemical signature.

Barroso-Alvão Pegmatitic Field

At the BA field it is possible to find different types of granitic pegmatite bodies, from barren to spodumene-, petalite-, and lepidolite-bearing pegmatites. These Li-rich bodies are located in the andalusite and biotite metamorphic zones, although a regional distribution of the various bodies is not clearly defined. The K/Rb medium values from bulk analysis are 9.80 for the lepidolite-rich pegmatites, 27.44 for the petalite-rich and 40.05 for the spodumene-rich bodies. Micas K/Rb medium values from petalite-rich are 51.50 and 15.76 for lepidolite-rich pegmatites.

Fregeneda-Almendra Pegmatitic Field

In contrast, at the FA field the pegmatite bodies show a zoned spatial distribution: barren pegmatites located near to the granitic complex and the Li-enriched bodies further away from the granite. The petalite-rich pegmatites occur at the andalusite-sillimanite metamorphic zone, whereas the spodumene-rich pegmatites appear in the biotite and/or chlorite isograd. The K/Rb medium values from bulk analysis are 10.49 for the lepidolite-rich pegmatites and 30.38 for the petalite-rich bodies. Micas K/Rb medium values from the petalite-rich are 69.74; 76.02 for the spodumene-rich and 15.86 for the lepidolite-rich pegmatites.

Final Remarks

Similarities in the petrography, mineralogy and geochemistry of the different types of pegmatites of both pegmatitic fields, as well as their spatial association with synorogenic peraluminous leucogranitic complexes of the same age and similar geochemical signature, and the alike metamorphic conditions, suggest that they could be related to similar petrogenetic processes.

Felsic magmas indicate crustal recycling during NAIP and FLIP formation

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Felsic magmas are typically subordinate compared to mafic magmas within large igneous provinces (LIPs). However, silicic melts do occur within most, if not all, the LIPs and they are locally voluminous or even dominant.

We investigated silicic volcanics of the Palaeogene North Atlantic Igneous Province (NAIP) and of the Mid-Jurassic Ferrar Large Igneous Province (FLIP), Antarctica.

In the NAIP, silicic magmas erupted at several stages of the volcanic evolution, most often preceding the mafic volcanics, but in other places contemporaneously with them. Available evidence indicates that felsic volcanic rocks in the NAIP are related to multiple eruptive centers or caldera complexes that are mainly concentrated along the rifted continental margins. Such an eruptive center was drilled during ODP Leg 104 Site 642E on the Vøring Plateau off Norway. The lower 130 m of that core are made up of glassy dacitic lavas and some minor basaltic andesitic lava flows with an interlayered rhyolitic ignimbrite. Their mineralogy and geochemistry characterize these felsic rocks as being derived from partial melting of metasedimentary rocks: they are calc-alkaline, strongly peraluminous ($Al/(Ca+Na+K) > 1.1$) and corundum normative, have high Th/Ta, La/Sm ratios, pronounced negative P and Ti anomalies, radiogenic isotope compositions ($^{87}Sr/^{86}Sr_i > 0.711$, $\epsilon Nd_i \sim -8$), high stable isotope values ($\delta^{18}O > +10\text{‰}$) and characteristic aluminium-rich minerals such as cordierite and mullite. The felsic magmas formed within an intra-continental rift setting at the location of an ancient suture zone and eventually lead to continental breakup.

In the FLIP, which extends along the cratonic margin of East Antarctica, the effusive section is underlain by 50 m of reworked rhyodacitic to rhyolitic fall-out tuffs (Shafer Peak Formation, SHF) originating from very distal large volume (ultraplinian), caldera-type eruptions, as they occurred synchronously in the Patagonian-Antarctic Peninsula Silicic Large Igneous Province. Whole rock geochemical analyses indicate that the SHF tuffs are strongly peraluminous and corundum normative, S-type crustal melts, most likely generated in a back-arc environment by underplating of large volumes of Ferrar LIP magmas.

A Mesoproterozoic Sm-Nd age for the Oddanchatram anorthosite massif, south India: Evidence for ancient crustal contamination and significance to the regional terrane assembly

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Within the Southern Granulite Terrane (SGT), S. India, the margin of the Archaean Dharwar craton demarcates an apparent suture zone between Late Archaean and Proterozoic terranes. This zone was intensely reworked in a collisional tectonic regime during the Neoproterozoic and is presently manifest as the deep-section of a crustal-scale shear zone system, the Palghat Cauvery Shear Zone (PCSZ), which separates terrains with Late Archaean. (ca. 2.5 Ga) granulite facies metamorphism from those with Neoproterozoic (ca. 0.55 Ga) granulite metamorphism. Charnockites from the Neoproterozoic domains indicate a complex map pattern of Archaean and Mesoproterozoic Sm-Nd model- T_{DM} ages and Meso- to Neoproterozoic zircon and monazite U-Pb ages. However, there is no clear evidence for Mesoproterozoic juvenile crust in the region.

The Oddanchatram anorthosite massif, an elongated oval shaped body (~ 80 km²) occurs within a steeply dipping shear zone that branches off from the PCSZ. It is composed largely of coarse grained metaanorthosite (avg. An=55%) in the core and deformed gabbroic anorthosite and norite along the margin. The suite is structurally concordant with deformed charnockite, garnet-sillimanite gneiss and granitoid units. A primary mineral assemblage of plagioclase (> 90 modal %), interstitial hornblende, pyroxene, zircon and titanite and a secondary assemblage of recrystallized high-calcic plagioclase with K-feldspar exsolution, garnet, biotite, and quartz characterize the anorthosites. Major and trace element compositions are consistent with plagioclase cumulates from a calc-alkaline mafic melt. Compared to model primitive mantle, the Oddanchatram suite is enriched in Sr, Eu and depleted in Nb, Ta, Zr and U. An Sm-Nd isochron gives an age of 1814±98 Ma (2 σ), ϵ_{Nd} = -11.7. Nd (T_{DM}) model ages range between 2.7 and 3.2 Ga, similar to those of the spatially associated charnockites. The relationship between Nd abundance and Nd- isotopic compositions suggest a significant crustal-contamination of a differentiated mafic parental melt involving Mid- to Late Archaean crust. Implications of such Mesoproterozoic crustal components (a possible anorthosite-mangerite-charnockite-granite association) to the regional terrane assembly in an orogenic setting is discussed.

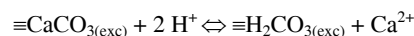
Proton/Calcium ion exchange behaviour of calcite: Implications for aqueous speciation and CO_{2(g)} sequestration

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The quantitative characterization of the proton sorptive properties of calcite in aqueous solutions has represented a major experimental challenge. In this study, we introduce a headspace-free closed-system titration technique that can quantitatively resolve sorption equilibria from dissolution/precipitation reactions and allowed us to investigate the proton sorptive behaviour of calcite at 25 ± 1° over a relatively wide range of chemical conditions (7.1 ≤ pH ≤ 9.5; 4·10⁻⁵ M ≤ ΣCa²⁺ ≤ 5.2·10⁻³ M; 1.3·10⁻⁴ M ≤ ΣCO₂ ≤ 1.8·10⁻² M and available reactive area: solution ratios from 0.2 to 5.7 m²/L) by means of acidimetric and calcium ion titrations.

A net proton uptake coupled with the incongruent release of Ca²⁺ over CO₃²⁻ ions, both largely exceeding the theoretical number of reactive sites available at the calcite surface, lead us to postulate that proton sorption extends beyond the calcite surface via a proton/calcium ion exchange mechanism with "labile exchangeable cation sites":



This reaction is represented by the empirical Langmuir-power exchange function:

$$K_{Exc} = \left(\frac{X_{\equiv\text{H}_2\text{CO}_{3(\text{exc})}}}{X_{\equiv\text{CaCO}_{3(\text{exc})}}} \right)^n \frac{(a\text{Ca}^{2+})}{(a\text{H}^+)^2}$$

where $n=1$ and $\log_{10} K_{Exc} = 12.96 \pm 0.21$. The implications of the proposed mechanism on aqueous speciation (e.g. pH buffering, control of the calcite saturation state) and CO_{2(g)} sequestration in carbonate-rock aquatic environments will be discussed.

Are Li, B and Sr-isotopes tracers for serpentinization?

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As new oceanic lithosphere is built up at mid-ocean ridges, fluid-rock interaction occurs. Bulk rock analyzes on altered spinel harzburgites from ODP leg 209 (Mid-Atlantic Ridge) showed that during serpentinization, light element content changes and influences strongly the light element abundances in the oceanic plate. This effect is supported by *in situ* mineral measurements (e.g. orthopyroxene looses B compare to bastite (polymorphe of serpentine)).

Interaction between the mantle and the ocean is not simple. During penetrating into the ocean plate fluid looses and gains elements. Therefore in most cases an evolved fluid is interacting with deeper lying, fresh rocks and leaves an evolved isotopic signature behind. Water-rock ratios, calculated on the base of ⁸⁷Sr/⁸⁶Sr -ratios (average 0.708726) in serpentinites from the MAR, indicate high fluid-rock interactions. The unusual high $\delta^{11}\text{B}$ content (+29.6 to +40.52‰) and normal to very low $\delta^7\text{Li}$ (-28.46 and +7.17‰), however, allowed us to model hydrothermal processes underneath a ridge. Our model suggests, that if equilibrium between fluid and rock occurs, the evolved fluid composition must be as high as +70 ($\delta^{11}\text{B}$) and the $\delta^7\text{Li}$ -composition of a similar evolved fluid would be as low as 0‰.

Our results show that at ODP leg 209, B, Li and Sr-isotopes can successfully be used to quantify reactions between seawater and very young oceanic mantle rocks. Low water-rock ratios lead to extremely high $\delta^{11}\text{B}$ and low $\delta^7\text{Li}$ values. This signature could potentially be transported into subduction zones. In general, however, the B, Li and Sr isotopic composition of altered oceanic mantle should be highly variable depending on water-rock ratios and on age.

Our current knowledge of the isotopic composition of Andean ice cores: New observations and modelling studies

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Greenland and Antarctic ice cores have provided a wealth of quantitative paleoclimate information both at orbital and millennial timescales. Motivated by the demonstrated potential of this polar archive, exploration of tropical ice cores started about 30 years ago in the tropical South American Andes, where high altitude glaciers contain well-preserved ice, suitable for paleoclimate investigations. The isotopic composition of Andean ice cores was measured using the same methods as those used for polar ice cores. In Antarctica, a robust relationship exists between surface temperature and the isotopic composition of snow. However, this temperature control breaks down for low latitudes, where cloud systems are dominantly of convective character and the influence of surface or near-surface temperature on the formation of precipitation becomes spurious. Spatially, a weak correlation between the isotopic composition and the amount of precipitation has been found in modern precipitation data. The atmospheric water cycle in the tropics is highly complex and thus our current knowledge about fractionating versus non-fractionating recycling, transpiration, partial evaporation of condensates and equilibrium with surrounding vapour is limited. There is no single controlling factor that dominates the impact of climate on the water isotopes and, consequently, there is a need for a full understanding of local and regional dynamic factors controlling the water isotopes.

Here, we present recent and new studies including both direct observations and modelling developments (mesoscale model, radiative-convective 1D model) that explore the different climate controls on the isotopic composition of Andean precipitation.

Coupled hydrological and geochemical modelling of a tropical watershed

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Tropical areas cover about 40% of the continental surfaces. They contribute between 30% and 50% to the global discharge to the ocean. We propose to model weathering fluxes and associated CO₂ consumption at a catchment scale in this environment. In South India, the Western Ghats make an orogenic barrier to the SW monsoon. It induces a sharp climatic gradient, defining three climatic zones from the West to the East: humid, sub-humid and semi-arid zones. An experimental watershed, Moole Hole, is currently monitored in the sub-humid zone since 2003 (ORE-BVET).

Weathering fluxes are simulated with a lumped hydrological model coupled with a geochemical model of weathering process (WITCH). The model boundary conditions are defined from field hydrological, mineralogical and chemical data. The particular climate, alternating long dry periods with short but intense precipitation events, provides a good test for the robustness of the geochemical model.

The first step in this modelling is to properly calibrate the hydrological model with runoff measurements using precipitation and evapotranspiration data as input. The second step is to generate current soil solutions, groundwater and river chemical contents. Results are compared with field data on a three year measurement period. The coupled model evaluates the CO₂ consumption by weathering and its possible *in situ* carbon sequestration due to precipitation of pedogenic carbonates.

The coupling of hydrological and geochemical model offers the possibility to simulate scenarios of weathering under a varying climate. It can be used to explore the impact of man-induced global climate change on tropical weathering processes (monsoon precipitations are expected to increase when global climate is warmer).

A CD-MUSIC surface complexation database for modeling oxyanion sorption on Iron oxyhydroxides

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We have developed an internally consistent surface complexation reaction database for the sorption of As(III), As(V), B(III), Cr(VI), Mo(VI), S(VI), Sb(III), Sb(V), Se(IV), Se(VI), and V(V) on goethite and HFO based on the CD-MUSIC model. Surface complex geometries and reaction stoichiometries were constrained by spectroscopic studies where available. CD values (Δz_0 and Δz_1) for the surface complexes were obtained from published *ab initio* studies or estimated from bond valence principles. Iron oxide surface site densities of 3.45 and 2.7 sites/nm² were used for singly and triply coordinated >Fe sites, respectively, and inner and outer layer capacitances 0.85 and 0.75 F/m² were assumed.

Equilibrium constants for the surface complexation reactions were retrieved from an extensive experimental dataset of oxyanion sorption on goethite and HFO compiled from the literature through 2007.

The CD-MUSIC database provides a consistent, description of oxyanion sorption on iron oxyhydroxides over a wide range of pH, sorption site density, and solution composition, and is particularly useful for geochemical modeling of competitive sorption in multicomponent systems.

As ^{III}	>FeOAs(OH) ₂ , (>FeO) ₂ AsOH
As ^V	>FeOAsO ₃ H, (>FeO) ₂ AsO ₂ , (>FeO) ₂ AsO ₂ H
B ^{III}	>FeOB(OH) ₂ , >FeOB(OH) ₃
Cr ^{VI}	>FeOCrO ₃ , (>FeO) ₂ CrO ₂
Mo ^{VI}	>FeOMo(OH) ₅ , >FeOMoO ₃
S ^{VI}	>FeOSO ₃ , >FeOSO ₃ H, (>FeO) ₂ SO ₂ , (>FeO) ₂ SO ₂ H
Sb ^{III}	>FeOSb(OH) ₂ , (>FeO) ₂ SbOH
Sb ^V	>FeOSb(OH) ₅ , (>FeO) ₂ Sb(OH) ₄
Se ^{IV}	>FeOSeO ₂ , >FeOSeO ₂ H, (>FeO) ₂ SeO, (>FeO) ₂ SeOH
Se ^{VI}	>FeOSeO ₃ , >FeOH ₂ SeO ₄ , (>FeO) ₂ SeO ₂
V ^V	(>FeO) ₂ VO

Table 1: Surface complex stoichiometries.

Mo isotopic composition of pelagic ooze from ODP Legs 198 and 208: Investigating a global signature

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Our Mo isotope analysis of various skeletal and non-skeletal carbonates has revealed a large fractionation in the ocean environment. It exceeds the $\delta^{98/95}\text{Mo}$ range of 3‰ defined by black shales and Fe-Mn oxy-hydroxides, i.e. the maximum variation found within the significant Mo sinks. It is thus important to characterize the isotopic signatures of different carbonate sinks and to determine the processes leading to the observed fractionation.

Here we present Mo-isotope data of pelagic ooze from ODP-Legs of Shatsky Rise, NW-Pacific and Walvis Ridge, S-Atlantic, documenting the last 70Ma. The isotopic variation is large (2.6‰), ranging from 1.2‰ down to -1.4‰. This is not in agreement with data obtained from contemporaneous Fe-Mn-crusts with uniformly light values of $\sim -0.7\text{‰}$, a result which has been interpreted to show that the ratio of oxic to anoxic sedimentation has not varied by more than 10% over the Cenozoic time [1]. However, as carbonate rocks represent $\ll 1\%$ of the global Mo sink the observed variations stored in the pelagic ooze do not require changes in the global Mo ocean inventory due to mass balance reasons. This favors the assumption that the hydroxides actually reflect a stable ocean-water Mo composition and that further fractionation mechanisms are responsible for the isotopic signature of the deep sea carbonates. Additionally, as the two ODP records correlate well from the Eocene through the Pleistocene, a globally acting mechanism that governs the isotopic signal is implied. Moreover, major changes in the global Mo isotope record are coeval with significant changes in the ocean circulation patterns. Our preliminary evaluation of factors responsible for the observed signature focuses on the global Cenozoic cooling trend and the closing of the Isthmus of Panama.

[1] Siebert *et al.* (2003) *EPSL* **211**, 159-171.

Chemistry of an antarctic subglacial environment: The role of subglacial geochemical processes in global biogeochemical cycles and quantifying subglacial hydrological processes

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Subglacial environments especially the availability of basal water plays an important role for the dynamic of ice sheets. Hydrological processes however are far from being understood as direct observations are hampered through kilometre-thick ice. Over the past years, it also has become more and more evident that despite the cold and isolation wet subglacial environments provide a viable habitat for life. Geochemical and biogeochemical processes in the sub ice environment not only can create and release chemical compounds, subglacial bio/geochemical processes may also play an important role in global geochemical cycles, like the global carbon cycle, or the cycling of iron and fertilization of the oceans.

Here we present the first geochemical measurements of the geochemical composition of basal water and pore water from beneath the West Antarctic Ice Sheet. Our results point towards an oxygen depleted environment in the Upstream C area (Kamb Ice Stream). Geochemical measurements conducted on the subglacial water and sediment also indicate the removal and transport of inorganic carbon from the subglacial environment to the oceans. This removal and transport may constitute a significant flux and release of inorganic carbon across the ice sheet grounding zone into the sub ice shelf cavity.

Our results also point out that subglacial environments are far from being understood and that sample recovery and *in situ* observations will be crucial for understanding subglacial environments and their role for ice sheet dynamic, the interaction between ice sheets, the underlying lithosphere and the oceans as well as the impact of subglacial processes on global geochemical cycles.

Denudation rate meters in mountain belts: Big brush or fine tip?

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Of the three meters that are in our hands for measuring the erosion and weathering (=denudation), basin-wide rates determined from cosmogenic ^{10}Be in river sediment have in the past years perhaps provided the most fundamental insights into the patterns at which mountains erode. The global picture is constantly changing by high-quality data that is now being produced from active belts with high erosion rates. The rates are very consistent within an individual range, and good correlations with basin characteristics such as altitude emerge from global compilations these rates. These rates also usually agree within a factor of two with those derived from thermochronology, hinting at some long-term stability or even geomorphic steady state. Unlike river loads with all their sometimes unpredictable short-term stochastic climate and land use forcing, cosmogenic nuclide-derived rates seem to record processes taking place over geologic time scales.

However, cosmogenic nuclide-derived rates have also produced their fair share of surprises, even contradicting previous geomorphic expectations. Some serious deviations from the global trends between denudation rates and basin characteristics emerge as ever closer looks are being made. For example basin studies in the Sierra Nevada and in the tropical Highlands of Sri Lanka have shown that it is active faults, not steep hillslopes per se that result in the fastest landscape denudation while the absence of active landscape rejuvenation results in slow denudation despite high rates of precipitation. In the European Central Alps denudation rates are high (> 1 mm/yr), and correlate stunningly well with rock uplift rates from leveling measurements, a real tectonic eye opener given that this part of the Alps is not even experiencing active convergence.

So it is the exceptions, based on individual basin-wide denudation rates, rather than the rules, that are telling us the real stories about the distinct tectonic, lithologic, or climatic processes that operate. If true, then the next steps are in identifying those small-scale settings where these driving forces can be singled out, combined with weathering indices, and can be associated with distinct rates of bedrock stream lowering, valley incision, channel hillslope coupling, soil production, and sediment storage.

In situ Hf Isotope analyses within individual zircon growth zones

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We have developed a micro-analytical technique for precise and accurate *in situ* measurement of Hf isotopes of zircons within individual growth zones using a multiple-collector inductively-coupled-plasma mass spectrometer (MC-ICPMS) connected to a single excimer laser-ablation system. In order to improve the accuracy of the Hf isotope ratio analysis, previously reported correction methods for isobaric interferences on ^{176}Hf by ^{176}Yb and ^{176}Lu were evaluated, and we found that only the use of independent mass bias factors for Hf and Yb in the isobaric interference correction lead to more reliable Hf isotope ratios.

The precision and accuracy of this method was evaluated using six well-known and widely used zircon standards (91500, Temora-2, GJ-1, Mud Tank, BR266 and Monastery). Analyses were carried out using spot sizes of 40 and 60 μm . The resulting Hf isotopic ratios of these six zircons are in agreement with reported values. In order to test the isobaric correction of ^{176}Hf we added different Yb solution during the ablation procedure, based on the knowledge that the Yb/Hf ratios of many common zircon grains increased up to 0.15.

To test the reliability of the Hf isotopic data of small zircon growth zones we selected samples from the Cretaceous belt of the Balkan Peninsula (Serbia, Bulgaria). *In situ* LA-ICPMS U-Pb dating analyses remain important to define the time of geological processes. Based on Hf isotope measurements of zircons, including Pb-Sr-Nd isotope tracing, we can demonstrate different crust/mantle evolution within the Cretaceous belt. *In situ* Hf measurements can demonstrate that the Lu/Hf system remains closed during younger metamorphic events; no change of the ϵHf values between core and rim is observed.

Metasomatism of the UHP Svartberget olivine-websterite body in the Western Gneiss Complex, Norway

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The Svartberget olivine-websterite is cut by fractures filled with websterites and garnetites. P-T estimates using standard geothermobarometric techniques cluster around 4.0 GPa at 800°C for the body and 5.5 GPa at 800°C for a fracture-filling websterite, confirmed by the presence of microdiamond. The bulk rock chemistry of the olivine websterite (wall rock) is intermediate between an ultramafic and mafic composition. Within the fractures a metasomatic column developed principally consisting of garnetite in the core and garnet-bearing phlogopite websterite towards the wall rock. Fluid immobile elements like Zr are transported to an extent that the garnetite in the core of the fractures have up to 300 ppm Zr. Age corrected initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the different metasomatic zones are clustering around 0.735. Even the most pristine remnants of the olivine-websterite (the wall rock) show signs of fluid/rock interaction e.g., in terms of high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.723). The most likely source for the metasomatic agent is the hosting felsic gneiss that shows many leucocratic pods and lenses. Samples from both gneiss and leucocratic lenses have Sr ratios as high as 0.750 and Zr contents up to 250 ppm.

In order to better understand the metasomatism of the Svartberget body numerical modelling is used to make a first order quantification of the dominant processes of element transport needed to produce the metasomatic column now present.

Is assimilation of sedimentary basement responsible for the temporal geochemical variations of Etna magmas?

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Mount Etna (Sicily, Italy) is located in a peculiar tectonic position between the colliding African and European Plates. The volcano is constructed on a 5 km thick succession of Meso-Cenozoic marine sediments (carbonate, marls and sandstones). Mt Etna volcanic rocks are characterized by complex spatial and temporal evolution. The oldest eruption products are of sub-alkaline tholeiitic lavas that evolved with time into Na-alkaline-type lavas. Many explanations have been brought forward to explain the geochemical composition, including mantle plume magmatism, subduction influenced magmatism and assimilation of crustal material. Although Etna belongs to one of the best studied volcanoes in the world, there is a lack of a complete data set on well dated rocks. In this new study we aim to disentangle the secular changes in composition by (1) obtaining precise Ar-Ar dates for good stratigraphic control, (2) investigating if assimilation of crustal material is an important process.

We present new major- and trace element Sr-Pb isotope data and precise Ar-Ar dates for 40 samples spanning the whole eruption history of Mt Etna. This sample set gives us for the first time precise stratigraphic control of processes occurring in the source of Etna and the magma chamber. We also analysed 10 sediments from the basement on which Etna is constructed. The sediments display significant variations in Sr and Pb isotopes ($^{87}\text{Sr}/^{86}\text{Sr}=0.708\text{-}0.786$, $^{206}\text{Pb}/^{204}\text{Pb}=18.6\text{-}19.8$). As previously reported by other studies, there is often Sr isotope disequilibrium between clinopyroxene and whole rock. In our study the maximum difference in $^{87}\text{Sr}/^{86}\text{Sr}$ between groundmass and clinopyroxene is 0.0002. This observation, coupled with detailed trace-element modelling, establishes that assimilation of material from the sedimentary basement is an important process. In addition, the precise Ar-Ar dates suggest that the role of crustal assimilation increases through time.

The effect of lead on the kinetics and mechanisms for the formation of hematite from ferrihydrite

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The crystallisation of hematite (HM) from 2-line ferrihydrite (FH) in the presence of lead was studied under alkaline condition at temperature between 160 and 240°C using synchrotron-based, *in situ* energy dispersive X-ray diffraction. The data showed that HM formed via a two-stage crystallisation process with goethite (GT) as an intermediate phase (Fig.1). In the first stage, HM and GT both formed from FH, whereas in the second stage HM crystallised from GT.

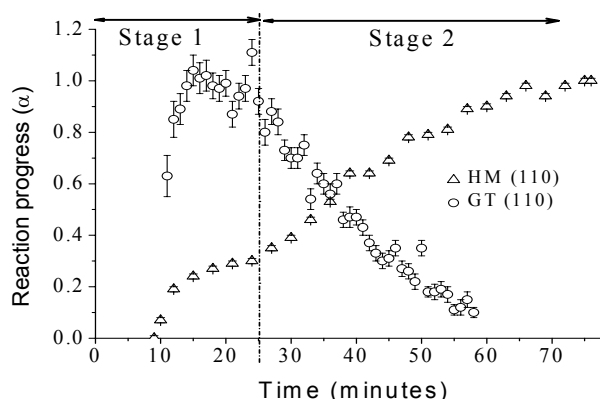


Figure 1: Reaction progress (α) for the FH to GT and HM reaction at 180°C.

The time-resolved data was fitted with the Johnson-Mehl-Avrami-Kolmogorov model (JMAK) [1] to extract rate constants and induction times. From the Arrhenius plots the activation energies of nucleation ($E_a(\text{nuc.})$) and crystallisation ($E_a(\text{cryst.})$) of HM in the first stage were 15.8 and 67.1 kJ/mol respectively, while the $E_a(\text{cryst.})$ in the second stage was 73.3 kJ/mol. Combining with previous studies [2, 3] an aqueous-aided 2D transformation mechanism is proposed for the HM crystallisation

When compared with the crystallization of HM from pure FH under equivalent conditions [3] the data showed that the presence of lead (20 mg Pb/ g FH) reduced the reaction rate by about one order of magnitude.

[1] Avrami (1939) *J. Chem. Phys.* **8**, 212-224. [2] Bao & Koch, (1999) *GCA* **63**, 599-613. [3] Shaw *et al.* (2005) *Am. Min.* **90**, 1852-1860.

Xenolith glasses: A key to deciphering mantle processes?

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Silicate glasses, common in mantle xenoliths from both continental and oceanic settings, have been variously interpreted in relation to processes that occur in the upper mantle or during transport to the surface. We studied here anhydrous and hydrous lherzolites from a continental setting (Massif Central, France) in which cryptic and modal metasomatism has been evidenced [1, 2], in order to test the potentiality of glasses for identifying the nature of the metasomatizing agent. Usually, minerals rather than glasses are used to study metasomatic processes, as the small size of the glasses makes the analysis difficult. However, the EMP procedure developed in our laboratory allows to analyze trace elements (Sr, La, Ce, Nd, Zr, Ti, Y) at the micro scale [3].

Fresh glasses occur as pockets in reaction zones between minerals or as thin veinlets along grain boundaries. The glass composition, which falls within that of world-wide mantle xenolith glasses, varies between the different xenoliths or within one single xenolith. In the hydrous samples, glassy pockets of clinopyroxene, olivine, spinel (\pm plagioclase) and formerly volatile-filled bubbles are frequently associated with amphibole. The amphibole breakdown exerts a major control on the glass composition, but an additional component is required in particular to account for the alkali budget. On discriminating major element plots [4], glasses from hydrous samples fall both within the alkali silicate- and carbonatite- related metasomatism fields (depending on the xenolith or on the glass settings in one xenolith), while glasses from anhydrous samples are related to a carbonatite metasomatism. However, the trace element signature may be in contradiction with the major element information.

Thus, caution is required in using the glass geochemical signature for elucidating mantle processes, and further studies of effects of melt-rock ratios on the composition of the metasomatic agent are needed.

[1] Wagner & Deloule (2007) *Geochim. Cosmochim. Acta* **71**, 4279-7296. [2] Bouhedja *et al.* (2002) 12th Goldschmidt Conf, *Geochim. Cosmochim. Acta.* A96. [3] Fialin *et al.* (1999) *Am. Mineral.* **84**, 70-77. [4] Coltorti *et al.* (2000) *Earth Planet. Sci. Letters* **183**, 303-320.