**Microbial life associated with low temperature alteration of ultramafic rocks in the Leka ophiolite complex**

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The Leka Ophiolite Complex (Mid-Norway) is a unique location for sampling oceanic crust and mantle lithologies. To examine peridotite-hosted subsurface microbial communities we have drill-sampled a dunite unit that is located close to ancient crust-mantle boundary. Samples were taken of mineralised fractures as well as of ground water produced by a 50 m deep borehole. Microbial community analyses were done by 16S rRNA gene sequence amplification clone library constructions. The morphological diversity was examined by electron microscopy. Enumeration of Archaea and Bacteria were done with fluorescent microscopy and real time polymerase chain reaction.

Different microbial communities were observed in the groundwater, the fracture fillings and the surface water. The groundwater, having a pH of 9.1, was dominated by close relatives of putative hydrogen oxidizing beta Proteobacteria suggesting that microbial communities at Leka are largely driven by hydrogen possibly produced by low temperature water-rock reactions. The microbial communities in the mineralised fractures are dominated by close relatives of heterotrophic hydrocarbon-degraders, but close relatives of hydrogen-, manganese-, and iron-oxidizers were also present.

**Metal-silicate mixing during impact-driven planet accretion – Implications for the age of the Moon**

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The final accretion of planet Earth involved giant collisions between proto-planets (>1000 km radius) with the Moon forming as a result of one of these impacts. At this stage both bodies had differentiated into a metallic core surrounded by a silicate mantle. During the Moon-forming impact nearly all metal sank into the Earth's core. We have investigated to which extent large self-gravitating iron cores can mix with surrounding silicate as they sink through the Earth's mantle. This allows us to evaluate how incomplete metal-silicate equilibration during core formation influences the short-lived chronometer, Hf-W, used to infer the age of the Moon.

We have established fluid dynamical models of turbulent mixing in fully liquid systems to constrain the degree of iron-silicate mixing. Erosion of sinking cores driven by Rayleigh-Taylor instability does lead to mixing, but only 1-20% of Earth's core would emulsify and equilibrate with the silicate mantle during Earth's entire accretion process. The initial speed and obliquity of impact is of little importance, but the size and shape of the sinking core matters. We evaluate the mixing potential for shear instabilities where silicate entrainment across vertical walls leads to mixing. The turbulent structure indicates that vortices remain at the largest scale and do not cascade down to centimeter length scales where diffusion operates and isotopes can equilibrate.

Because most of the impacting metal plunge directly through the silicate mantle, and the fraction of impacting metal that mix within diffusion distance from silicate is small, giant impacts have limited effect on siderophile depletion during core formation. On a global scale residual 182W from early core formation processes is left behind in the mantle and this source of 182W generates a higher tW excess compared to what is expected in early models for 182W evolution in the silicate Earth. Hence, the Moon forming impact must have occurred >30 Myrs after CAI formation. Furthermore, we find that a single giant impact has limited ability to reset the Hf-W system and that tW is more sensitive to early core formation processes than to radiogenic ingrowth after the giant impact [1].

Effects of mining on groundwater quality in Gaft Chromite Mine, Iran
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Effluent from chromite mines due to extraction activities into aquatic systems is an environmental issue [1, 2]. To investigate the effects of chromite extraction on the groundwater quality in Gaft Chromite Mine, water samples were taken from the mine area.

Due to basic condition of the tunnel effluent (pH=9.74), solubility of most ions decreased [3, 4] and thus EC, total hardness, and concentration of ions in tunnel effluent were similar to the upstream groundwater as well as groundwater in the mine site [Fig.1]. In other words, mining activities had no adverse effect on the water quality of the region although it slightly increased the concentration of Cr (VI) in the groundwater in the mine site. The concentrations of Cr (IV) in water samples were 0.04, 0.04, 0.06 and 0.02 (all in mg/L) in upstream and downstream groundwater, groundwater in the mine site, and tunnel effluent respectively. Because of the geochemical condition downstream of the mine [5], the reduction in the pH of downstream groundwater (pH=8.13), the concentration of bicarbonate, chloride, calcium, magnesium, and sodium ions as well as the total hardness and EC in downstream groundwater (4 Km far) were increased.

Figure 1: Concentration of ions in water samples.


Zircon Hf-O isotope evidence for crust-mantle interaction during continental deep subduction
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In situ SIMS zircon U-Pb dating and O isotope analysis as well as LA-(MC)-ICPMS zircon U-Pb dating and Lu-Hf isotope analysis were carried out for postcollisional mafic-ultramafic rocks in the Dabie orogen, China. The zircon-U-Pb dating gives consistent ages of 126±1 to 131±1 Ma for magma crystallization. Survival of residual zircon cores is identified by CL imaging and U-Pb dating, yielding ages of 697±10 and 770±11 Ma that agree with protolith ages of UHP metagneous rocks in the orogen. Zircon Hf-O isotope compositions show systematic variations that can be categorized into three groups. Group I has the lowest δ18O values of 2.0 to 2.9‰ but the highest εHf(t) values of -6.3 to 1.1 with the youngest Hf model ages of 1.1 to 1.6 Ga. Group II displays intermediate δ18O values of 4.0 to 5.1‰ and εHf(t) values of -29.0 to -9.9 with Hf model ages of 1.8 to 3.0 Ga. Group III exhibits the highest δ18O values of 5.2 to 7.3‰ but the lowest εHf(t) values of -33.7 to -18.2 with the oldest Hf model ages of 2.3 to 3.3 Ga. The three groups of Hf-O isotope compositions correspond to a three-layer Hf-O isotope structure in the subducted continental crust, suggesting its involvement in the mantle source. Along with existing data for whole-rock Sr-Nd isotopes and trace elements, it appears that the mantle source for the postcollisional mafic-ultramafic rocks is characterized by fertile lithochemistry, the continental crust-like signature of trace elements, the heterogeneous enrichment of radiogenic isotopes, the differential incorporation of supracrustal materials, and the variable concentrations of water. Clearly, such a source is neither the asthenospheric mantle nor the refractory subcontinental lithospheric mantle (SCLM). It is a kind of orogenic SCLM that would be generated by reaction of the overlying SCLM peridotite with hydrous silicate melts derived from the different layers of subducted continental crust. Therefore, the postcollisional mafic-ultramafic rocks provide a petrological record of crust-mantle interaction during the continental deep subduction. Melt-peridotite reaction is hypothesized to take place in the Triassic to generate the mantle source of pyroxenite and hornblendite, which underwent partial melting in the Early Cretaceous to cause the mafic-ultramafic magmatism.
The Biodegradation of [omim][PF₆] with activated sludge in anoxic conditions

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Many Ionic Liquids have significant solubility in water, which can result in the potential problems with degradation or persistence in environment. Biodegradation is the microbial breakdown of chemical compounds, such as Ionic Liquids. Compared to chemical or physical methods, it seems to be more environmentally friendly. This study focuses on the biodegradation efficiency and the pathways of [omim][PF₆] under anoxic conditions. Biodegradation efficiency of [omim][PF₆] under anoxic conditions was studied by acclimatizing the activated sludge with the UASB reactor. The proposal of possible metabolic pathways of [omim]⁺ in anoxic conditions was analyzed by identification of the breakdown products using GC-MS. The biodegradation experiments were also performed under aerobic conditions. It suggests faster flow enhanced the contact frequency of [omim][PF₆] and microbe, but was not conducive to the removal rate with the increase of run-time. The results showed that the [omim][PF₆] removal efficiency reached the highest as the flow velocity of UASB was 0.75 mL·min⁻¹ in this study. The molecular weights of the main degradation products were 83, 155, 102, 170 and 109, respectively. It is predicted that there were 3 main pathways for anoxic biodegradation of [omim]⁺, which were different from the aerobic process because of the different electron acceptor. Similar to the aerobic process, N—C bond ruptured first, but the metabolism of [omim]⁺ did not appear to undergo oxidation reactions but reduction reactions in anoxic conditions. The toxicity of the breakdown products was reduced under anoxic conditions according to their polarities and EC₅₀ in references.

Acknowledgements: This research was financially supported the National Science & Technology Pillar Program during the Eleventh Five-Year Plan of China (2009BADC2B01-01)

Controls on and effects of surface ocean oxygenation prior to the Great Oxidation

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Multiple lines of evidence suggest that organisms that produced free oxygen had evolved by ~2.7Ga, while geochemical evidence shows pervasive oxygenation of ocean margins prior to the Great Oxidation Event (GOE) at 2.4Ga [1]. However, given the likely heterogeneous spatial distribution of environments supporting oxygen-producing ecosystems, it is unclear whether oxygen production would have resulted in a significant flux to the atmosphere, or remained a local phenomenon restricted to “oxygen oases” in the surface ocean or mat-based environments. Here we use a combination of ocean GCM and box-model coupled atmosphere-ocean-ecosystem studies, in combination with constraints from proxy data, to investigate: (i) factors controlling the prevalence of surface ocean oxygenation prior to the GOE, (ii) the (local) geochemical signature of early oxygenic photosynthesis in different environments (i.e., restricted to shelf seas, or widespread in the surface ocean), and (iii) the likely impacts on atmospheric oxygen, including constraints on the relative timing of the evolution of oxygen photosynthesis relative to the GOE.

As an initial geochemical diagnostic for spatial structure we focus on factors controlling the production of isotopically light organic carbon via methane recycling. We show that oxygenation of the surface ocean could have been widespread in upwelling regions, that consumption of oxygen in the surface ocean increases stability of a low atmospheric pO₂ state, and that aerobic methanotrophy in open environments produces only relatively small changes in δ¹³C insufficient to explain the excursions seen at ~2.7Ga [2] which would then require a different mechanism and most likely restricted environments.

Chemical and isotopic composition of Lower Vindhyan organic rich sediments: Role of chemical alteration and grain size distribution

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Several grey and black shales samples from the Lower Vindhyan section in the Central India have been collected. The samples have been chosen to represent various degrees of chemical alteration; those collected from the surface are extensively weathered whereas those collected from deeper in the mine cuts are relatively fresh. These samples have been analyzed for major ion composition, C\textsubscript{org} and $\delta^{13}$C of bulk organic matter.

The major ion compositions indicate influence of both chemical alteration and grain size distributions driven by mineralogical sorting. Abundances of bulk organic content (C\textsubscript{org}) show significant positive correlation with Na/Al and an inverse correlation with K/Na. In contrast, C\textsubscript{org} exhibits a weak positive correlation with Si/Al. Together, these observations indicate that organic carbon content in these samples are controlled by various degrees of chemical alteration and that the influence of grain size distributions and mineralogical sorting may be rather weak. It is unclear to what extent the original relationship between the grain size and C\textsubscript{org} has been lost by chemical alteration.

Carbon isotopic composition ($\delta^{13}$C) of bulk organic matter shows a significant positive correlation with (1/C\textsubscript{org}). A first order interpretation of this trend is that relatively fresh organic matter is characterized by more negative $\delta^{13}$C values whereas less negative $\delta^{13}$C values represent organic matter that are altered by exchanging carbon with the weathering solution. Our results are in contrast to those observed by Van Os \textit{et al.} [1]. Abundances of specific organic compounds, a suite of trace elements and grain size distributions would be measured to better understand the role of chemical alteration, grain size distributions and specific organic compounds in influencing the abundances of metals, organic carbon and carbon isotope composition of organic matter of these organic rich sediments.


XPS heating with mass spectrometry: Tackling chalk, coccolith and calcite surfaces

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Chalk hosts significant quantities of the North Sea oil and biogenic calcite (CaCO\textsubscript{3}) is a major component of the chalk. The biogenic calcite is in the form of coccoliths, precipitated by some species of single-celled marine algae. To understand the complex recrystallisation behavior of natural chalk, biogenic calcite is often used as a model system. Abiogenic calcite is also used as a proxy for chalk during surface reactivity studies\textsuperscript{1}.

In this study to examine similarities and differences between the biogenic and abiogenic calcite surfaces, we used X-ray photoelectron spectoscopy (XPS), coupled with an \textit{in situ} residual gas analyzer (RGA), to examine natural chalk, cultured coccoliths and natural abiogenic calcite (Iceland Spar). We characterised, compared and contrasted the surface of the natural and model systems before, during and after heating to 500°C. The samples were heated to mimic reservoir conditions and to investigate the kinetics of the decarbonation reaction.

High resolution carbon 1s (C 1s) XPS spectra of the samples show differences in the surface composition. All samples display C-C bonds at 285.0 and CO\textsubscript{3} bonds at 290.1 eV. In addition, the chalk and coccoliths contain water-rich inclusions and these ‘explode’ during heating, producing spikes in the mass spectrometer data. No evidence of inclusions exist in the chalk or coccolith samples, which release H\textsubscript{2}O and CO\textsubscript{2} at a more constant rate. During the heating experiments, the COOH coatings are removed from the surfaces of the coccoliths and chalk, and the surface composition becomes more similar to the abiogenic calcite. Ongoing work will examine sample reactivity, including dissolution rates of chalk and coccolith surfaces before and after heating.

[1] Bovet \textit{et al.} (2011) \textit{This Issue}.
A Late Triassic major negative $\delta^{13}$C spike linked to Wrangellia LIP: The Carnian Pluvial Event revealed

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During the Carnian (Late Triassic) a major climatic and biotic change is known, namely the Carnian Pluvial Event (CPE) [1]. This event is characterized by more humid conditions testified by hygrophytic palynological assemblages and palaeosols typical of humid climates; the crisis of rimmed carbonate platforms, a rise of the CCD and the increase of siliciclastic input across the western Tethyan realm; high extinction rates among ammonoids, crinoids, bryozoans and conodonts [2] and the first occurrences of dinosaurs and calcareous nannoplankton [3]. The CPE is similar in age to the conodonts [2] and the first occurrences of dinosaurs and ammonoids, crinoids, bryozoans and conodonts [2] and the first occurrences of dinosaurs and calcareous nannoplankton [3]. The CPE is similar in age to the eruption of Wrangellia large igneous province (LIP) [3], an oceanic plateau outcropping in western North America. Here we report an abrupt negative $\delta^{13}$C shift at the onset of the CPE: high and low molecular weight n-alkanes, isoprenoid lipids and total organic carbon (TOC) show a sharp 2‰ - 4‰ negative carbon isotope excursion (CIE) that testify for a rapid sequestration by coal swamps after the end-Permian mass extinction [4]. We propose that this CIE was caused by an injection of light C by the Wrangellia volcanism into the reservoirs of the exogenic C-cycle with strong consequences for climate and biota.


Widespread evidence for heterogeneous accretion of the terrestrial planets and planetisimals

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The abundance and relative proportion of highly siderophile elements (HSEs) in Earth’s mantle deviate from those predicted by low-pressure equilibrium partitioning between metal and silicate during formation of the core. For many elements, high-pressure equilibration in a deep molten silicate layer (or ‘magma ocean’) may account for this discrepancy [1], but some highly siderophile element abundances demand the late addition, a ‘late veneer’, of extraterrestrial material (i.e. heterogeneous accretion) after core formation was complete [2]. Siderophile elements in smaller asteroidal bodies will not be affected by high-pressure metal-silicate equilibration and so, with highly efficient core formation, may be absent, significant differences in the proportions of HSEs can be anticipated.

Here we present new HSE abundance and $^{187}$Os/$^{188}$Os isotope data for basaltic meteorites, the HEDs (howardites, eucrites and diogenites thought to sample the asteroid 4 Vesta), anomalous eucrites (considered to be from distinct Vesta-like parent bodies) angrites and aubrites (from unidentified parent bodies) and SNCs (thought to be from Mars). Our data, taken with those for lunar rocks [4], demonstrate that these igneous meteorites all formed from mantle sources that possessed chondritic (i.e. primitive solar system) elemental and isotope compositions, indicating that late accretion is not unique to Earth, but is a common feature of differentiated planets and asteroidal bodies. Variations in the total HSE abundance suggest that the proportion of ‘late veneer’ added is a simple consequence of the size of each body (cross-section and/or gravitational-attraction), and may account for the volatile element budget, and the oxidation-state of Earth, Mars, the Moon and Vesta.

Transport of endocrine disruptive compounds in Hawaiian soils

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The release of endocrine disruptive compounds (EDCs) into the environment is of increasing concern due to their impact on freshwater organisms, ecosystem sustainability and human health. Several studies have emphasized that extended exposure to low concentration of some hormones can alter the endocrine and reproductive systems of aquatic animals. This study was conducted to investigate the transport behavior of two natural EDCs (17 beta estradiol, E2 and estrone, E1) in several Hawaiian soils under different experimental conditions. Soils collected in Hawaii showed higher content of mineral oxides, such as iron and manganese oxides compared to most soils in the continental US. Batch sorption and column leaching experiments were used to better understand the fate of both chemicals.

During batch experiments, equilibrium conditions were reached within 12 hours. In all soils having E2 only, its loss occurred due to sorption and degradation. Microbial degradation was inhibited using sodium azide. 100 mg/L azide alone did not completely stop degradation of E2. It was unclear whether this loss was due to microbes or partially due to abiotic mechanisms.

Column experiments showed that with E2 only, E1 was constantly present, showing the degradation of E2 to E1 despite the addition of a sodium azide. For different soils (5 total), breakthrough curves (BTC) of E1 and E2 appeared after the BTC of bromide, suggesting the presence of sorption process during the transport of estrogens through the soil matrix. Facilitated transport was mostly observed in presence of volcanic ash soil. The presence of recycled water enhanced the transport of estrogens in all the different soils. Early appearance of peaks, long tails and complete recovery (mass balance) of both estrogens was more pronounced in transport studies involving the recycled water. Non-equilibrium conditions were observed during the study, especially in presence of undisturbed soil when flow interruption occurred. These conditions were mostly related to the presence of macropores in the soil. Macropores were able to reduce the contact time between soils and estrogens, facilitating their transport.

The oxygen isotopic composition of xenoliths from Tallante (Southern Spain): Evidence for crust recycling into the mantle

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Mantle xenoliths from Tallante (Betic Cordillera, Spain) include samples recording a peculiar distinct style of metasomatism that induced orthopyroxene, plagioclase, phlogopite and amphibole crystallization and generated “hydrous” opx-rich mantle domains. The latter are locally crosscut by felsic veinlets containing plagioclase and orthopyroxene ± quartz ± phlogopite ± amphibole. The observed parageneses and available Sr-Nd-Hf isotopic data suggest that metasomatic agents were related to recycled of crust components within the mantle, plausibly in connection with subduction processes occurred during the Cenozoic Betic orogenic cycle.

In this study we investigated representative samples of composite xenoliths consisting of peridotite crosscut by felsic veins (varying in size from centimetric to millimetric) and unveined peridotites, measuring the 18O/16O ratios of the constituent minerals by laser fluorination. Results show that the narrow O-isotope compositional “typical” of mantle rocks, and the limited oxygen isotope fractionation at mantle temperatures, make oxygen isotopes a powerful tool for identifying recycled crustal material in the mantle. Orthopyroxene and plagioclase of the centimetric vein show δ18O values of +9.8 and +10.6‰, respectively, whereas clinopyroxene of the surrounding peridotite country rock has δ18O= +6.2‰. Plagioclase of two distinct millimetric felsic veins show δ18O of 7.6 and 7.3‰. The δ18O values significantly higher than typical mantle ones provide insights to the genesis of the Cenozoic subduction-related magmas of the Betic region that include silica-oversaturated calcalkaline (s.l.) and lamproite products, possibly resolving source vs. shallow level crustal contamination of the magmatic rocks. Moreover, the different O-isotope composition recorded in veinlets characterized by different thickness could provide insights into diffusion-assisted O-isotope reequilibration of mantle rocks, thus constraining the time for “crust digestion” into the mantle.
How do plant emissions affect atmospheric nanoparticle formation?

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Non- and semivolatile compounds, produced by the oxidation of atmospheric trace gases that are emitted by human and biological activity, can undergo a phase transition and enter the atmospheric aerosol phase, either onto existing particles or forming new nanosized condensation nuclei. The most likely candidates of precursors of aerosol number-producing vapors are sulphur dioxide and plant-originated volatile organic compounds.

Currently, the controlling mechanism of tropospheric nanoparticle formation is still an open question. Field and laboratory measurements have clearly indicated a strong correlation between observed sulphuric acid – a product of SO2 oxidation – and nanoparticle concentrations and formation rates (eg. [1]). On the other hand, observed seasonality and comparisons with plant VOC emission strengths show that aerosol formation is also correlated with biogenic organic oxidation. Laboratory studies with real plant emissions have shown a clear dependence of aerosol formation on the VOC emission strength and also the chemical mixture ([2, 3]), thereby ruling out the possibility that nanoparticle formation by nucleation would be completely independent of organic compounds.

We investigated the formation of nanosized condensation nuclei (nano-CN) from sulphuric acid and plant emissions in the Jülich Plant Chamber setup. We performed a series of experiments using boreal forest tree emissions at levels commonly found in the boreal boundary layer.

We found that while the variation of the VOC concentration had a strong impact on the gas phase chemistry and also the hydroxyl radical and sulphuric acid levels, the changes in particle formation rates were not explainable by sulphuric acid concentration variations alone, but the particle formation process is directly influenced by the plant emissions.


Estimating mantle temperature from a global comparison of seismic models and the petrology of mid-ocean-ridge basalts

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Inferring mantle temperature and composition is one of the primary applications of seismic tomography. Mantle temperature and composition also strongly influence the petrology of mid-ocean-ridge basalts (MORBs) erupted on the seafloor. It is therefore reasonable to hypothesize that a relationship exists between seismological and petrological data. We have investigated whether such a relationship does exist using global seismic models and a new and expanded global compilation of MORB major-element chemistry. Petrological data obtained from PetDB form the core of our geochemical database, which is augmented by unpublished analyses and Iceland samples from GEOROC. We correct all measured values to 8% MgO and determine the mean composition for 231 individual ridge segments. We compare the petrological data (ridge depth, Na8, Fe8, etc.) with global mantle models of shear-wave speed, attenuation, and transition-zone topography. Ridge depth and wave speeds at 200-400 km depth are correlated globally, suggesting that the same factors that control ridge depth and crustal thickness also influence seismic velocity. For several ridges, anti-correlation between ridge depth and depth to the 410-km discontinuity is seen, in particular the Southwest Indian Ridge and the Mid-Atlantic Ridge. The comparisons also reveal correlation between Na8 and shear-wave speed at 200-300 km globally. Comparison of the petrological data and mantle seismic models provides an opportunity to understand the connection between temperature and composition at depth and the processes occurring at the surface.
Xenoliths reveal lower crustal deformation and metamorphism with no obvious surface expression

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Lower crustal xenoliths afford an opportunity to investigate the crustal architecture in 3D and to test whether deformational and metamorphic events in the lower crust are coupled to those known from outcrop studies.

Within the Iapetus Suture Zone (ISZ) in Ireland, where Laurentia and Avalonia collided obliquely during the c. 420 Ma Caledonian Orogeny, Carboniferous magmatism has transported granulite-facies lower crustal xenoliths at several localities. The xenoliths are predominantly metasedimentary and on seismic and geochemical grounds provide a near-perfect match with present-day lower crust [1, 2]. Thermobarometry indicates original depths of c. 22-33 km, and temperatures in the range 700 - 900 °C [1]. Ion microprobe U-Pb zircon dating of syn-tectonic granitic leucosomes in metasedimentary xenoliths indicates at least three discrete high-grade metamorphic events (382 ± 2 Ma, 373 ± 3 Ma and 360 ± 3 Ma), all younger than Caledonian. The oldest corresponds to an episode of Middle Devonian volcanism and may be related to syn-sedimentary extension. However, the younger events have no deformational or thermal effects known at outcrop. They demonstrate that ductile deformation and melting took place c. 25 km below the surface without significant surface expression suggesting significant mechanical and thermal decoupling of the lower and upper crust.


Glaucophane-bearing metabasites from the East Sayan (Russia):
Composition and origin

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Glaucophane-bearing metabasites in the East Sayan are known as Okinsky blueschist belt. In one of the small massifs PGE mineralization was established. This massif is presented by latitudinal strike body, which contained by greenschist strata. Basic and ultrabasic rocks are altered to amphibolites, epidote-actinolite-amphibolic rocks and serpentinites, which most fractured and rich by asbestos veinlets. Further small pyroxenite bodies, gabbro and herzolite relics are detected. Amphiboles are presented by three varieties. At first has a dark-green to light-brown color diagnosed as ferrichermakite, at second has light-blue color – vinchite, ferribarruasite, at third presenting as violet-color margin is a magnoriebeckite. From the center to outside direction Na-content increases whereas Ca and Al contents are decrease. PGE is concentrated by extensive zones of pyrite-magnetite mineralized amphibolites and sulfidized garnet-diopside-chloritic rodingites. Ore minerals are presented by magnetite with rare ilmenite relics, hematite, rutile, cassiterite and sulfides which form single areas and presented by pyrite, chalcopyrite, zigenite, arsenopyrite, sphalerite, galena. Noble metal minerals are native gold, mercurian gold, Cu-bearing gold. Platinum-Group element (PGE) minerals are presented by sperrylite. Concentrations of noble metals in ores attain to Au – up to 1.47 ppm, Pt – up to 5.2 ppm, Pd – up to 0.55 ppm. Obtained P-T conditions of metabasite formation correspond to P>8 kbar, T – 250 - 300°C are indicate it’s formation in the subduction zone or accretion wedge. Island-arc complexes are characterized by mercury and tin deposit presence, where ore-forming elements are entered from mantle fluids. These fluids also contain noble metal, incoming by the mantle ultrabasic rocks partial melting.
The peculiaritys of Khasurta massif rocks formation on the melt inclusion study (Angaro-Vitim batholith, Western Transbaikalia)

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The Khasurta pluton (about 900 km²) presents early phase of the Angara-Vitim batholith formation. On the south this pluton is overlapped by Mesozoic and Cenozoic deposits of the Udinskaya intermontane trough, on the north it is limited by a regional break, and on the east and west it intrudes Proterozoic - Early Cambrian volcano-terrigenous and terrigene-carbonaceous sediments. As a whole the pluton is in discordant contact with surrounding rocks.

The pluton’s interior is not homogenous and consists of monzonitic and granosyenitic rocks. As a rule surrounding carbonaceous rocks are substituted by scarns in contact with the pluton.

Zircon grains were selected from monzonites. Zircon grain sizes of - up to 1 mm in length, they often form intergrowths. Small crystals (200 - 600 microns) have a zircon habit, and a light pink color.

Melt inclusions in zircon grains from monzonites were studied. A composition of ungomogenized melt inclusions was analysed using the electron microscope (LEO 1430 VP), have been identified: quartz, K feldspar, plagioclase, apatite, muscovite.

Six experiments each with a duration of about 1-3 hours at different temperatures (800-1000°C) were carried out (inclusions size – 4-10 µm). Using an electron microscope the composition of the three homogenized inclusions has been studied. Its composition is more acidic as compared with monzonite and has increased Na, K content.

Thus, based on these results we conclude that Khgasurta massif rock crystallisation temperature was more than 920°C. Monzonites are represent acid (“sienitic”) magmas cumulates. High Na and K content permit to suggest monzonite affiliation to the shoshonitic series.

Study was supported by Lavrentievsky grant SB RAS.

Radiochemical analysis of environmental radioactivity for surveillance and characterization

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Great changes have been achieved in the world politics and economics with the development of nuclear science and technology. However, many problems in the sustainable developing of society and potential risks to the ecology have been also aroused by radioactive pollution. To assess the risk of radionuclides in environment, not only the total amount but also the biogeochemical behavior, the origin and the diffusion (migration) path of these radioactive pollutants in environment need to know. For this purpose, radiochemical analytical methods are keys to characterization of radioactivity.

Since 1990s, inductively coupled plasma mass spectrometry (ICP-MS) has been widely used for monitoring trace radionuclide and identifying the source terms for different environment samples, including soil, underground water, plants and air [1]. In our laboratory, different analytical methods based on ICP-MS measurement and radiochemical separation have been developed to monitor and characterize radionuclides in environment. This work aims to summarize the newly developed analytical methods using UTEVA extraction chromatography combined with ICP-MS for monitoring transuranium nuclides in soil [2] and a direct aerosol measurement attempt with ICP-MS for determining the radionuclide concentration in air [3]. Meanwhile, the result of an environmental radioactivity investigation will be presented to show the bioavailability of radionuclides of different origin [4], as well as the radioactivity transfer from soil to plant. In addition, the developed methods to identify nuclear materials by isotopic signature and age determination have also been well shown with satisfactory result [5]. However, tackle for very low level contamination and for deliberately mixed material is still a challenge to work on.

High-pressure microbiology in the synchrotron light

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The Earth’s subsurface is characterized by hostile conditions for life in terms of temperature, pressure and nutrient availability. Although our current view of the biosphere extension is restricted to shallow geological depths, deep life may encounter pressures of hundreds MPa. As an important microbial energetic process, dissimilatory metal reduction needed to be investigated as a function of pressure.

We measured the effects of pressure on the reduction of Se(IV) and Fe(III) to Se(0) and Fe(II), respectively by the bacterial model Shewanella oneidensis MR-1. This strain is a mesophilic and piezosensitive counterpart of psychrophilic and piezophilic Shewanella representatives that have been frequently isolated from deep-sea environments. Kinetics and yields of Se(IV) and Fe(III) reduction were monitored in situ by X-ray Absorption Spectroscopy (XAS) in an autoclave optimized for in situ XAS measurements [1]. Most measurements were performed at the BM30B beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Early measurements on the reduction of Se(IV) were also performed in diamond anvil cell at the ID22 beamline of the ESRF.

Metal reduction occurs in cultures of MR-1 at pressures in excess of 100 MPa. This shows that the metabolic activity of a microbe, despite being piezosensitive, extends far beyond its pressure limits for growth here at 50 MPa. Consequently, considering only the ability to grow in the conditions of the deep subsurface as a proof of metabolic activity may lead to an underestimation of the impact of the biosphere in deep environments. Although the exact experimental conditions do not mimic complex subsurface environments, we show here that the metabolic activity of a surface microbe potentially brought to the deep subsurface can affect significantly biogeochemical cycles as those of selenium, but more importantly those of iron and carbon.


Subduction factory unroofed: Modern submarine magmatism in the North Fiji Basin, Southwest Pacific

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An extensional setting at the southern termination of the North Fiji Backarc Basin (southwest Pacific), which occurs in response to westward roll-back of the Vanuatu trench and eastward roll-back of the Tonga trench, allows subduction-related magmas to reach the surface (seafloor) with only a minimal extent of both fractionation and crustal contamination, thus providing a unique insight into magma generation processes with the subduction factory.

Volcanic rocks collected within this area during the SS10/2004, SS08/2006 and SS03/2009 voyages of the R/V “Southern Surveyor” reveal a large spectrum of subduction-related magma compositions from backarc basin basalts to boninites, calc-alkaline basalts and high-Mg adakites. All magma series have very primitive, high MgO endmembers, which contain abundant high-magnesian olivine phenocrysts (Fo 92-94) formed during the earliest stages of melt evolution. The data reveal that melts produced due to adiabatic decompression of the mantle wedge play an important role in magma genesis. Within the studied area, a number of such melts can be identified which differ in both the extent of the contribution of the subduction-derived components, and the extent of depletion of the mantle source. Also abundant are melts produced by melting of the basaltic component of the subducted oceanic crust, which extensively re-equilibrate with the surrounding mantle during their ascent to the surface. These melts are also characterised by a range of compositions, range from low-Si, high-Mg to high-Si, high-Mg adakites. There is clear petrographic and geochemical evidence for extensive mixing between high-Mg adakitic and backarc basin magmas in this area, which results in formation of primitive magmas with typical calc-alkaline and boninitic affinities. Our results suggest that in less extensional settings, where unfractionated magmas rarely reach the surface, the role of this mixing in the genesis of typical calc-alkaline magmas may be more difficult to identify, however it may play an important role in subduction-related magma genesis in general.
Application of the correspondence analysis to determine anomalous elements and samples

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Determination of the anomaly elements and samples

Based on the soil lithogeochemistry samples were taken from a probable porphyritic Cu-Au mineralized area, the mineralized elements and anomalous samples were identified [1,2,3]. For this propose, a correspondence analysis was done on a matrix of 29 elements (columns) and 149 samples (rows) from the study area. According to the correspondence analysis, a final matrix of 28 factors or variables (columns) and 29+149 labels (rows), which includes of elements and sample numbers, was calculated. The cross plots of two variables (Fig. 1 A and B) from the final matrix were confirmed Au and Cu as anomaly elements and numbers 40, 74, 22 and 84 as anomalous samples.

Figure 1: Correspondence analysis for identification of the anomalous element and samples

Conclusion

Identification of the anomaly sample numbers and anomaly elements could be possible by using the correspondence analysis. The combination of this method and anomaly separation method could separate the high potential area for follow up exploration program.


Large-area input, inventories, and transport of $^{129}$I and $^{127}$I in Germany

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The environmental abundance of $^{129}$I has been changed substantially, mainly as a consequence of the $^{129}$I releases from European reprocessing plants. The stable $^{127}$I and the long-lived $^{129}$I exhibit massive disequilibria in all biotic and abiotic compartments of the environment in Western Europe. Measurements of $^{127}$I and $^{129}$I in some German soils revealed $^{127}$I/$^{129}$I ratios of $10^{-2}$ to $10^{-10}$ [1, 2], whereas the $^{127}$I/$^{129}$I ratio in a pre-nuclear Russian soil was found to be $5.7 \times 10^{-12}$ [3]. Iodine from wet and dry precipitation is accumulated in soils, transported by surface waters, infiltrates groundwater, and makes its way through the biosphere. Many of the ecological pathways of iodine are still unknown.

The goal of this project is to investigate the continuous atmospheric input via dry and wet deposition, the inventories in the pedosphere and the output by river waters of $^{129}$I and $^{127}$I in entire Germany.

To this end, aerosol filter samples from 4 locations will be analysed, as well as precipitation samples from 10 locations, and surface water samples from 15 locations along the major rivers in Germany. Sampling is supported by DWD (German Meteorological Service), BfG (Federal Institute for Hydrology), PTB (Federal Metrology Institute), and BfS (Federal Office for Radiation Protection). Additionally, sampling of different soil types at various locations in Germany, down to a depth of 50 cm, is in progress.

Deposition rates, deposition densities and transport rates will be calculated using inductivity coupled plasma mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS) as analytical tools. First results from the two-year sampling, which startet in March 2011, will be shown. A sufficiently dense grid of sampling points will allow a nationwide mapping of the atmospheric input, the accumulation in soils, and the transport with surface waters back to the sea. Based on these data, a model will be established describing the different pathways of iodine isotopes in the environment.

[2] Daraoui et al. (2011) to be submitted to J. Environ. Rad
Formation of Platinum-Group Minerals from an evolving sulfide liquid at Sudbury, Canada

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Chalcophile and platinum-group elements (PGE) are collected by a magmatic sulfide liquid and form PGE (± Ni-Cu) deposits. Early-crystallizing monosulfide solid solution (MSS) concentrates Os, Ir, Ru and Rh (IPGE) and the residual liquid concentrates Cu, Pt, Pd, Ag, As, Bi, Te, and Sn. It is important to determine the host phases of the PGE, which are sulfide minerals and/or platinum-group minerals (PGM), in order to understand the petrogenesis of the deposit and to improve PGE extraction. Previous work shows that PGM form by:

1) exsolution from base metal sulfides, 2) crystallization from the residual Cu-rich liquid and/or a late-stage immiscible melt and 3) remobilization during metamorphism or by hydrothermal fluids.

We have investigated the origin of PGM from Sudbury Ni-Cu-PGE deposits by combining a PGM study with whole-rock data and laser ablation-ICP-MS analysis of the sulfides. We found that a large proportion of the PGE are hosted in As-, Bi-, Te- and Sn-rich PGM, which formed over a wide range of temperatures during the evolution of the sulfide deposit. The amount of As in the initial sulfide melt, which varied according to the As content of the assimilated country rocks, was critical in determining whether As-PGM (IrAsS, RhAsS ± PtAs2) crystallized early (1200-900°C) from the sulfide liquid together with MSS. An As-rich sulfide melt crystallizes sulfarsenides so that the co-existing MSS is depleted in Ir and Rh whereas an As-poor sulfide melt does not crystallize sulfarsenides and the IPGE remain in MSS. The amount of Bi, Te and Sn increases during sulfide fractionation so that the following Pt-Pd-minerals crystallized from the residual liquid. Solitary grains of Pd, Sn and PtSn crystallized early (1300-800°C) from the Cu-rich sulfide liquid whereas an unnamed Pt(Sn,Bi)Te phase together with numerous Pt-Pd-Bi-Te-Ag minerals crystallized as composite grains from micro-droplets of an immiscible late-stage melt (1000-600°C). The small amount of Pt, Pd, Bi and Te, which partitioned into MSS, later exsolved (< 600°C) as laths of (PtPd)(BiTe)2 and PdBiTe and were remobilized during greenschist metamorphism.

Probable Mars atmospheric changes by the proposed terraforming process with silicon utilizing organisms

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The silicon utilizing organisms particularly diatoms are well known to tolerate different stress as evidenced in studies on past mass extinctions on Earth and also in artificial laboratory conditions. Thus these organisms may be utilized in terraforming suitable solar system objects and such proposals have already been given for Mars and the Moon [1] and further proposals are likely to be placed for Venus, Callisto, Europa, Ganymede, Enceladus and Titan in near future. In Mars, after initiation of such a terraforming process, by application of these organisms on the surface among basalts, clays, ice etc., a target oxygen level of 150 m bar in the atmosphere may reach within 500 years, with expected significant increase in nitrogen to 300 m bar and decline of carbon dioxide to as low as 10 m bar. As most solar radiations usually reach the surface of Mars, these organisms are expected to grow even at a low temperature in a surface pressure of 6-7 m bar. High carbon dioxide levels will affect the growth, fluorescence, pigmentation and carbonic anhydrase activity of these organisms with involvement of chlorophyll a, chlorophyll c and fucoxanthin. Presence of diverse genes is essential for proper terraforming process with organisms, mainly for efficient management of C and N. Thus a set of such organisms may be chosen for initial terraforming process according to gene library matching. Iron present on Mars surface has also a pivotal role in controlling carbon uptake by these organisms and regulating atmospheric partial pressure of carbon dioxide. Finally atmospheric erosion and escape processes particularly solar wind ion or proton and magnetospheric-plasma-driven sweeping may alter the expected values to some extent.

Silicate melting in the Earth’s deep upper mantle caused by C-O-H volatiles

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The onset of silicate melting in the Earth’s upper mantle influences the thermal evolution of the planet, geochemical differentiation of the interior, flux of key volatiles to the exosphere, and geophysical properties of the mantle. Although the first initiation of melting beneath mid oceanic ridges likely produces dry carbonatite melt as deep as ~350 km, owing to vanishingly small volume (~0.03%), its effect on geochemical and geophysical properties of the mantle is unclear. Geophysical data, however, suggest possible presence of partial melts to depths exceeding 200 km. Silicate melts have better prospects in this respect owing to higher viscosities and densities; however, they are not thought to be generated at depths approaching or in excess of 200 km. Here we present experiments in natural peridotite+CO2 systems over 2 to 5 GPa and constrain the location and the slope of the onset of silicate melting (melts with ≤25 wt.% CO2) in a carbonated mantle. We show that the P-T slope of transition from carbonate to silicate melt is steeper than the solidus of volatile-free peridotite owing to diminishing non-ideality of mixing between carbonate and silicate melt components as a function of pressure. This causes carbonated silicate melting of dry peridotite beneath ridges to commence as deep as ~230 km. Taking into account 50-200 ppm water in the nominally anhydrous mantle and its effect on freezing point depression, the onset of silicate melting for a sub-ridge mantle with ~100 ppm CO2 becomes as deep as ~260-300 km. Deep carbonated silicate melting can deplete the mantle from its water storage capacity, to match the depleted mantle water content beneath ridges. Deep onset of silicate melting also restricts the stability of carbonatite in the Earth’s deep upper mantle and the inventory of carbon and other highly incompatible elements at ridges becomes almost entirely controlled by flux of deep, wet carbonated silicate melts.

Finally, deeper transition from carbonatite to carbonated silicate melts causes the melt CO2 to be diluted at greater depths than previously modeled. This causes graphite to carbonated melt transition depth beneath continents to be deeper than recent estimates.

SHRIMP U-Pb geochronology of Neoproterozoic Rio Una sequence, NE Brazil, and the Rodinia break-up

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The amalgamation of Gondwana resulted from the fragmentation of Rodinia and the reassembly of the cratonic blocks during the Neoproterozoic. The Borborema Province is the western part of a major Brasiliano belt that extends from Brazil through NW Africa in pre-drift reconstructions. This province results from the convergence and collision among the West African, Congo-São Francisco, and Amazonia land masses about 600 Ma. The Rio Una Sequence is located within the PEAL Domain of the Borborema Province. It is comprised by 3 units. We are presenting U-Pb dating of the unit 1. This unit comprises migmatized metapelites with peraluminous mesossome (andaluzite-, cordierite-, garnet-bearing biotite gneisses), with quartzites intercalations. The studied sample was collected near one of these intercalations. The analyzed sample shows zircon grains with length ranging from 80µm up to 200µm. They are elongate to rounded, with aspect ratio ranging from 1:1 to 2:1. They usually show oscillatory zoning, and in some case a narrow metamorphic overgrowth. The 232Th/238U ratio of almost all analysed grains ranges from 0.20 to 2.16, suggesting that they come from an igneous protolith, or from a recycled igneous rock. The analyzed sample shows zircon grains with length ranging from 80µm up to 200µm. They are elongate to rounded zircons, with aspect ratio ranging from 1:1 to 2:1. They usually show oscillatory zoning, and in some case a narrow metamorphic overgrowth. The 232Th/238U ratio of almost all analysed grains ranges from 0.20 to 2.16, suggesting that they come from an igneous protolith, or from a recycled igneous rock. The U-Pb data with less than 5% discordance cluster mostly in the intervals 850-1100 Ma and 1800-2100 Ma. The data points that the unit 1 show a maximum depositional age of 854Ma. The age of this sequence is coeval with the age attributed to the beginning of the Rodinia break-up.
Mechanisms of copper immobilization by bacteria during precipitation of iron oxides

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This project focuses on interactions between bacteria and iron oxides, and the effects of such interactions on the behaviour of dissolved copper ions. Laboratory experiments were performed to track the fate of dissolved copper and iron during the gradual, incremental oxidation of dissolved Fe(II) and precipitation of iron oxide in the presence of Anoxybacillus flavithermus cells. The experimental data reveal significant and complex controls on copper immobilization, related to progressive changes in 1) ratio of copper to dissolved Fe(II) concentration, inferred to result from competition for bacterial sorption sites; 2) ratio of precipitated iron oxide to bacteria, inferred to result from desorption of Fe(II) initially associated with the bacterial surface; and 3) reaction time, inferred to result from increasing quantities of biogenic dissolved organic matter. Surface complexation models are developed to describe the experimental data. This study demonstrates that the immobilization of metal cations in bacteria-bearing settings should not be examined independently of progressive oxidation, hydrolysis and precipitation of iron.

Mars as a planetary oligarch

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There is considerable uncertainty as to how and when Mars formed [1,2]. In particular, its small mass compared to Earth and Venus is difficult to explain and some have suggested that Mars could be a stranded planetary embryo (also called an oligarch) that escaped collision and merging with other embryos [3]. A diagnostic parameter to assess this idea is its accretion time, which can be calculated using 182Hf-182W systematics of martian meteorites [2,4]. Unfortunately, the Hf/W ratio of the martian mantle is very uncertain, resulting in model age estimates that range between 0 to 15 My after solar system birth. To better constrain the Hf/W ratio of the martian mantle, we have measured the concentrations of Lu, Hf, U, Th by isotope dilution, as well as 182Hf/183Hf isotopic ratios of 43 chondrites from all major groups of chondrites [the methodology is described in ref. 5].

We estimate the Hf/W atomic ratio of the martian mantle to be 3.51±0.45. Using this Hf/W ratio, the measured value of \(\varepsilon^{182}\text{W}_{\text{Mars mantle}}=+2.6\) [2,4] can only be reproduced with an accretion timescale of ~2 Myr [6]. This is consistent with a stranded planetary embryo origin for Mars. Objects formed in the first few million years of the formation of the solar system would have incorporated enough 26Al to melt. We thus demonstrate that a magma ocean powered by 26Al-decay must have been present on early Mars. This changes our perspective on the formation of our planet as we have now identified a sample of the embryonic material that the Earth was made of. For example, Earth may have inherited its missing Xe problem [7] from a Mars-like precursor.

Linking solution composition and surface topography to the rate and mechanisms of diopside dissolution

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Whereas the dissolution rate of silicate minerals has been extensively studied at far-from-equilibrium conditions, extrapolating such rates over a broad range of solution composition has proven challenging. Regarding diopside, recent studies [1, 2] suggested that below 125 °C, an unexpected drop of the rate occurred for Gibbs free energies of reaction (ΔG°) as low as –76 kJ.mol⁻¹, with severe consequences on our ability to predict the rate of complex processes such as carbonation reactions [2].

The mechanism responsible for such a drop remains unclear and therefore needs to be deciphered. An examination of our previous data [2] led us to envisage that two different, non-exclusive aspects were worth investigating: (i) the possible passivating ability of interfacial, nm-thick Si-rich surface layers developed on weathered silicate surface, and (ii) the growth of etch pits formation on crystal surface, which were found to be responsible for drops of olivine [3] and albite [4] dissolution rates, respectively.

Our ongoing experiments aim at better constraining these two mechanisms, and determining in turn whether one of them could explain the above-mentioned drop of diopside dissolution rate. Classical flow-through experiments with controlled SiO₂(aq) concentrations are combined with both ex situ AFM measurements and in situ monitoring of the topography of the dissolving surface of diopside in a hydrothermal AFM flow-cell (e.g. [5]). By investigating the dissolution of several cleavages, we will show how these latter techniques represent a powerful tool for studying the anisotropy of diopside dissolution, and determining which face ultimately controls its dissolution rate. An attempt to link these observations to macroscopic determination of diopside dissolution rates as a function of fluid composition will be discussed.


Zone of Anomalous Mantle

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The most striking characteristic of both the Siberian and Slave diamond fields is their linear distribution. The concept of the “Corridor of Hope” was introduced [1] to refer to a northwest trend that appears to have controlled the emplacement of the most significantly diamondiferous kimberlites of the Slave craton. With displaced northern [2, 3] and southern extensions the corridor is 2300 km long.

The Siberian diamond fields have a linear distribution over 1000 km with one offset. The linear is described [4] as a “Zone of Anomalous Mantle” and mantle xenoliths and xenocrysts [5] show that Hartsburgite makes up a significant part of the lower mantle below 190-240 km thick lithospheric Archean terrane to the south but is missing beneath 125 km thick lithospheric Proterozoic terrane to the north.

Helmstaedt [6] proposed a model for the Slave craton in which Paleoproterozoic lithosphere has underplated Mesoproterozoic lithosphere beneath the corridor and the upper edge of the underplating Proterozoic is 270 km west of the corridor and controls the geometry of the corridor. Significantly Mirny is 250 km NW of the Akitkan Proterozoic fold belt and there is evidence [7] for a Proterozoic fold belt 250 km east of the Alakit/Daldyn/Muna diamond fields.

A modified 2.0-0.8 Ga reconstruction of the Proterozoic Supercontinent [8] has the Siberian “Zone of Anomalous Mantle” lined up with the N American corridor.

Conclusion

Proterozoic lithosphere underplated an Archean craton (Siberia & N America) on its Pacific ocean side that resulted in a single zone of anomalous mantle. Except where the zone was cut by the Akit Proterozoic orogenic belt that separated, thinned and destroyed the base of the adjoining Siberian and N American (Alaska North Slope) cratons, it is extremely favourable for hosting diamondiferous kimberlites.


Mineralogical Magazine  www.minersoc.org
Dynamical constraints on mantle reservoirs through time

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It is now generally accepted that Earth formed hot, due particularly to a giant, moon-forming impact late in accretion. A resulting magma ocean probably cooled on a geologically short timescale, and may not have left a strongly differentiated mantle, due to vigorous internal mixing, except possibly in the D" region. Loss of excess initial mantle heat would have taken ~0.5 Gyr. Core cooling is controlled by mantle plumes and may always have been slow. Plume activity may have been 2-8 times stronger during the Hadean and early Archean.

The Earth’s surface would have cooled early, soon after the last giant impact (~4.45 Ga?). An active mantle would be expected to produce mafic crust at a substantial rate, and this may have tended to founder episodically, possibly in large bodies. Conceivably some of these persist in D".

Gravitational settling of foundered or subducted mafic crust could have left the upper mantle strongly depleted, explaining isotopic evidence of stronger early depletion of incompatible elements. This upper mantle would produce only a thin mafic crust, which would facilitate an early start to plate tectonics and efficient cooling of the mantle.

A ‘basalt barrier’ may have formed within the transition zone, yielding a cool upper mantle and a hot lower mantle. Episodic breakdown and overturn of this stratified mantle during the first 1-2 Gyr could have volcanically resurfaced much of the planet.

An accumulation of denser mafic material in D" probably formed early. This persists strongly to the present, though it might not be able to form now. It could retain a record of major melting events from throughout Earth history.

No other mantle stratification is plausible at present. A putative thick layer in the lower mantle should produce mantle plumes several times stronger than what is observed, so it is unlikely.

Lithologic heterogeneity of the mantle probably formed early from foundering differentiated material. Much of the mantle complement of incompatible elements may be carried in hybrid pyroxenite, formed by reaction of melt from mafic inclusions with surrounding peridotite. Noble gases plausibly persist from the early Earth in this material, and the present mantle complement of incompatibles may be 2-3 times previous estimates, whose assumptions make them lower bounds.

Dynamical geochemistry

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Despite progress in reconciling important aspects of mantle chemistry with dynamics, mass balances of key elements and observations of noble gases have remained enigmatic. Resolution may follow from taking fuller account of the lithological heterogeneity of the mantle [1].

The Hofmann-White-Christensen reconciliation of refractory trace elements and their isotopes with the dynamical mantle has been strengthened by work over the past decade. The apparent age of lead isotopes and the broad refractory-element differences among and between ocean island basalts (OIBs) and mid-ocean ridge basalts (MORBs) can now be quantitatively accounted for with some assurance.

Noble gases may reside in a so-called hybrid pyroxenite assemblage that is the result of melt from fusible pods reacting with surrounding refractory peridotite and refreezing. Hybrid pyroxenite that rises off-axis may not remelt and erupt at MORs, so its volatile constituents would recirculate within the mantle. Hybrid pyroxenite is likely to be denser than average mantle, and thus some would tend to settle in the D" zone at the base of the mantle, along with some old subducted oceanic crust. Residence times in D" are longer, so the hybrid pyroxenite there would be less degassed. Plumes would sample both the degassed, enriched old oceanic crust and the gasy, moderately enriched hybrid pyroxenite and deliver them to OIBs. This model can account quantitatively for the main He, Ne and Ar isotopic observations, and for the poor correlation of unradiogenic gases with refractory-element enrichment in OIBs.

The difficulty with mass balances can be traced to the common inference that the MORB source is strongly depleted of incompatible elements. However conventional estimates focus on an ill-defined “depleted” mantle component while neglecting less common enriched components. Recent estimates have also been tied to the composition of peridotites, but these probably do not reflect the full complement of incompatible elements in the heterogeneous mantle. New estimates that account for enriched mantle components can satisfy mass balance requirements, although some additional uncertainties apply to argon. The result is that the MORB source is depleted by only about a factor of 2, relative to the primitive Earth.

Approaching the final frontier in lateral resolution for isotopic and chemical analysis with CHILI

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There is a clear need for improvements in lateral resolution and sensitivity beyond what is available with current state-of-the-art secondary ion mass spectrometry (SIMS) instruments. SIMS lateral resolution has reached ~50 nm and useful yields are at most a few percent. We are completing construction of CHILI (the CHicago Instrument for Laser Ionization), a resonant ionization mass spectrometry (RIMS) nanobeam instrument designed for isotopic and chemical analysis at the few-nm scale with a useful yield of 35–50% [1]. CHILI is equipped with a COBRA-FIB high resolution liquid metal ion gun (LMIG) and an e-CLIPSE Plus field emission electron gun from Orsay Physics, each of which can be focused to <4 nm. The electron gun will be used for secondary electron imaging, as the built-in optical microscope is diffraction-limited to ~0.5 µm. A piezoelectric stage capable of reproducible nm-scale motions and equipped with a sample holder that will accept a wide variety of sample mounts is operational. The flight tube for the time-of-flight mass spectrometer mounted vertically above the sample chamber; this assembly is mounted in the center of an H-shaped laser table equipped with active vibration cancellation devices. The table has been demonstrated to have a vertical vibrational amplitude of less than 0.2 nm. Resonant ionization will be done with six Ti:sapphire tunable solid state lasers pumped with three 40W Nd:YLF lasers, which will allow two to three elements to be analyzed simultaneously. Ion detection in existing RIMS instruments [2,3] is done with a microchannel plate with a single anode. Isotope ratio precision is limited by counting statistics, as no more than one ion of the most abundant isotope of an element can be counted for each pulse. CHILI will initially be equipped with such a detector, but we are developing a multianode detector to significantly improve the count-rate capability.

Partitioning of first-row transition elements between peridotite and melt

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To constrain possible lithologies in source regions of OIB [1–3], we experimentally determined partitioning of first-row transition elements (FRTE), Ga, and Ge between minerals in garnet peridotite and near-solidus partial melt at 3 GPa using LA-ICP-MS. K_{Mn-Fe}^D between peridotite and melt is ~1, so low-degree partial melts of peridotite inherit Fe/Mn of their source, similar to the results of previous studies [1]. K_{Zn-Fe}^D between peridotite and melt is 0.80, lower than previously determined from intermineral partitioning in natural peridotites (0.85–1) [3], primarily due to a lower measured K_{Zn-Fe}^OPX for opx (0.77 rather than 0.96). Most peridotite xenoliths have (Zn/Fe)^* from 4–12 [4], thus partial melts of peridotite may have (Zn/Fe)^* ratios as great as 15. Most primitive OIB have (Zn/Fe)^* from 10–15 [4], so derivation from a peridotite source can only be ruled out for a very few OIB lavas based solely on Zn/Fe. A fertile peridotite with 0.2 wt.% TiO_2 can generate a near-solidus melt with ~3.3% TiO_2. OIB with >3.3% TiO_2 require a non-peridotite or metasomatized source.

<table>
<thead>
<tr>
<th>D_{Fe}</th>
<th>D_{Co}</th>
<th>D_{Zn}</th>
<th>D_{Ga}</th>
<th>D_{Ge}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.86</td>
<td>0.062</td>
<td>0.65</td>
<td>4.1</td>
<td>0.81</td>
</tr>
<tr>
<td>0.81</td>
<td>1.8</td>
<td>0.65</td>
<td>0.15</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Table 1: Bulk perid./melt partition coefficients averaged from four experiments (assumed mineral mode: 60.8% olivine, 7.7% opx, 22.6% cpx, 8.9% garnet).

A coupled ion exchange, surface complexation, calcite dissolution, and mass transfer model to describe uranium(VI) desorption and reactive transport at the Rifle (USA) field site

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Predicting uranium mobility in the subsurface requires detailed knowledge of geochemical processes controlling the sorption dynamics of U(VI). This is a particular challenge in cases where aqueous solution conditions are highly variable. Desorption of U(VI) from mineral surfaces is strongly dependent on aqueous chemistry (e.g., pH, HCO3 and Ca concentrations). Further, kinetic processes such as intragranular diffusion affecting U(VI) desorption equilibrium may become increasingly important under conditions where changing solution chemistry causes relatively steep U(VI) concentration gradients.

In this research we have quantified the effects of aquifer sediment properties on the transport dynamics of U(VI) under variable chemical conditions and developed a reactive transport model that can be applied to field settings. An ion exchange model was calibrated first in experiments conducted with the aquifer sediment <2 mm fraction with calcite removed. This was then applied in combination with a surface complexation model to describe U(VI) transport in laboratory columns. Chemical conditions within the columns were varied through the injection of influent solutions with differing pH, bicarbonate, and major ion concentrations. Initial conditions within the columns were impacted by slow calcite dissolution. Stopflow events during column elution demonstrated U(VI) desorption was not at local equilibrium, and U(VI) elution data were used to calibrate a distributed rate mass transfer model for U(VI) desorption, at flow rates and alkalinity concentrations relevant to the Rifle site. Oversaturation with respect to calcite was observed in this column experiment and in the Rifle aquifer. In a column experiment with high influent bicarbonate, calcite oversaturation exceeded one order of magnitude, suggesting calcite nucleation and precipitation and U(VI) co-precipitation within the column. The model was successfully applied to describe field injection experiments after correction for local surface sediment properties (surface area, ion exchange capacity, and initial adsorbed U(VI)).

Geochemistry of granites from magmatic-metamorphic complex of Boein-Miandasht, Sanandaj-Sirjan Zone, Iran

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Geological Setting and sample description

The granitic plutons crop out the north of the Boein – Miandasht city: they intruded into the metamorphic rocks. Various ages have been assigned to the metamorphic complex: Precambrian [1], Paleozoic and Mesozoic [2]. Metamorphic rocks in the study area comprise phyllite, mica schist, amphibolite, marble and meta-rhyolite with minor quartzite. Alkali granite is the major rock type in the plutons. It is composed of quartz, K- feldspar, plagioclase, biotite, amphibole, epidote, allanite, zircon, sphene, magnetite, fumaraline and apatite.

Discussion and Results

The granites have contents of SiO2, ranging from 68.7 to 73.3%. They have high alkalis, with K2O = 2.3 to 5.01% and Na2O = 3.75 to 5.0%, but low Fe2O3 (0.8 - 1.7%), FeO (1.1-1.9%), MnO (<0.1%), MgO (0.4-0.7%), CaO (0.9-1.8%), TiO2 (0.3-0.5%) and P2O5 (0.1-0.2%). Al2O3 ranges from 13.8% to 14.9%.

Similarly the trace element compositions exhibit significant variations, particularly in the case of Rb (146.7-212.8 ppm), Y (32.1–40.2 ppm), Sr (65.3–153.0 ppm), Ba (400–633ppm), Ga (18.0-20.0 ppm) and high field-strength elements (HFSE) (Nb: 15.6–27.4 ppm; Ta: 1.5–2.4ppm; Zr: 184.3–346.0 ppm; Hf: 5.2–10.1 ppm). The granites display the characteristics of A-type granitoids. According to a geochemical classification scheme for granitoids, proposed by Frost et al. [3], the granitic rocks belong to ferroan, alkali-calcic, mildly peraluminous granites. The plot of Zr + Nb + Ce vs. 1000*Ga/Al suggest an A-type to fractionated granites character for the rocks. The granites show A2 field on ternary diagrams from Eby [4].

Molecular characterization of archaeal lipids across a hypersaline gradient

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Four halophilic archaeal strains, H. utahensis, N. pharaonis, H. sulfurifontis and H. gomorrense, were grown at a range of salinities (10-30% NaCl, w/v)). These strains represent four archaeal genera and have a range of salinity optima. Molecular analysis of membrane lipids in each strain by GC-MS revealed structures consistent with saturated, unsaturated and polyunsaturated dialkyl glycerol diethers (DGDs) of both phytanyl (C20) and sesterpanyl (C25) isoprenoid chains. In addition, we observed three trends: (1) the percentage of unsaturated DGDs increased with increasing NaCl concentration in the growth medium; (2) strains with a higher optimal NaCl concentration had a higher percentage of unsaturated DGDs; and (3) C25-C20 DGDs occurred in the two strains with higher optimal NaCl concentrations, N. pharaonis and H. utahensis. The strong linear correlation between optimal growth salinity and the amount of unsaturated DGDs (Fig. 1) suggests that the degree of membrane lipid unsaturation is an important adaptation to specific salinity niches in archaeal halophiles. Thus, halophilic archaea may regulate membrane lipid unsaturation in response to environmental salinity changes regardless of their salinity optima.

Figure 1: Average fraction of unsaturated DGDs versus optimal % NaCl (w/v) for four halophilic archaeal strains.

O and Ca isotopes in calcite grown under cave-analogue conditions

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Speleothem oxygen isotopes and growth rates are valuable proxies for reconstructing climate history. However, oxygen isotopes and growth rate are controlled by diverse environmental variables (including the climatically important variables rainfall and temperature) and there is a paucity of laboratory experiments to quantify the influence of these variables on speleothem chemistry. Quantitative data from such studies would dramatically improve our ability to reconstruct palaeoclimate from stalagmites.

We have completed a new series of carbonate growth-experiments in karst-analogue conditions in the laboratory [1,4]. The setup closely mimics natural processes (e.g. precipitation driven by CO2-degassing, low ionic strength solution, thin solution film) but with a tight control on growth conditions (temperature, pCO2, drip rate, calcite saturation index and the composition of the initial solution).

We derive a relationship between growth mass, temperature and drip rate, whilst in a more qualitative sense we observe a wider diameter of calcite growth with increased drip rate. δ18O results show that speleothem growth from fast dripping, cold settings are most favourable for palaeoclimate work. δ18O and δ44/42Ca provide important insight into the mechanisms of stable isotope fractionation in speleothems, which we discuss in the context of surface entrapment controlling Ca and O isotopic fractionation [2, 3]. Collectively, these experiments therefore provide a more robust understanding of the way that stalagmite carbonate responds to climatically important environmental variables.

Ru/Ir (Kane = 1.4± 0.2; Gakkel = 1.6± 0.6; SWIR = 1.5± 0.3; abundances, although all ridges studied have supra-chondritic peridotites. Abyssal peridotites analyzed in this study have ultra-slow spreading Gakkel, versus Indian or Atlantic ridge segments, are broadly similar (0.007±2‰). Unlike PUM, there is no systematic supra-chondritic CI- CIR = 1.4± 0.1), similar to estimates for primitive upper mantle (PUM). Unlike PUM, there is no systematic supra-chondritic HSE abundances in mantle (PUM). The HSE are in approximately chondritic -relative abundance data for bulk samples of abyssal peridotites from the Arctic (Gakkel), Indian (central [CIR] and southwest [SWIR]), and Atlantic (Kane) ridges.

Peridotites from the global suite range from relatively fresh to serpentinized harzburgites and lherzolites, with no systematic variation observed for HSE abundances or 186,187Os/188Os with alteration. Average HSE abundances of different ridge segments are broadly similar (0.007±2 × CI-chondrite). The HSE are in approximately chondritic-relative abundances, although all ridges studied have supra-chondritic Ru/Ir (Kane = 1.4±0.2; Gakkel = 1.6±0.6; SWIR = 1.5±0.3; CIR = 1.4±0.1), similar to estimates for primitive upper mantle (PUM). Unlike PUM, there is no systematic supra-chondritic Pd/Os in SWIR, CIR, or the majority of Gakkel peridotites. There is greater HSE abundance variability in ultra-slow spreading Gakkel, versus Indian or Atlantic peridotites. Abyssal peridotites analyzed in this study have 186Os/188Os ratios ranging from 0.1217 to 0.1587. The 186Os/188Os of SWIR peridotites (0.1198358±4), which were affected by the Bouvet hotspot at ~20Ma, are, on average, higher than for CIR (0.1198360±5), Kane (0.1198353±7) [1], and Gakkel peridotites (0.1198332±6). SWIR show a general positive correlation for 187Os/188Os-186Os/188Os, but no other correlations are observed between these ratios in the dataset. If CIR, Kane and Gakkel peridotites are representative of convecting upper mantle, then this reservoir has evolved with time-integrated Pt/Os, how this signature is transferred from the hotspot to the peridotites is unclear. Lack of correlation between Pt/Os and 186Os/188Os values relate to high time-integrated Pt/Os, how this signature is transferred from the hotspot to the peridotites is unclear. Lack of correlation between Pt/Os and 186Os/188Os for the suites suggests abyssal peridotites do not record absolute and relative abundances of the HSE in the convecting upper mantle with high fidelity.

Metasomatism beneath the Kerguelen Plateau associated with heterogeneous mantle plume

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The Kerguelen Plateau, in the Southern part of the Indian Ocean, represents the second largest igneous province on Earth. Its main emerging feature is the Kerguelen Archipelago, located in the Northern part of the plateau (NKP). Basic and ultrabasic xenoliths are commonly found disseminated within alkaline lava series, especially in the Southern and South-East part of the archipelago. The xenoliths were formed in PT conditions generally comprised between 0.75 to 1.6 GPa and 880 to 1010°C, corresponding to lithospheric conditions [1]. The xenoliths thus provide a unique opportunity to understand the processes that occurred during the construction of the NKP.

While there is no evidence for contamination of the xenoliths from their host lavas during their ascent, the xenoliths are metasomatized, as showed by the presence of both silicate and carbonate melt inclusions [2], and enrichment in incompatible trace elements [1]. In light of the comparable isotopic signatures for the Kerguelen alkaline volcanism and the xenoliths, the origin of this metasomatism, both silicate and carbonatitic-silicate melts, seems related to the Kerguelen Mantle Plume itself [3]. Using various types of xenoliths, we show here that (i) the metasomatism event is ~40 million years old, corresponding to the onset of the interaction between the South-East Indian Ridge and the Kerguelen mantle plume [4], and (ii) the two metasomatic melts can be distinguished using both trace element and isotope ratios. As such, xenoliths metasomatized by carbonatic-silicate melts have (Sm/Yb)N < 1, and 206Pb/204Pb < 18.200. Using Nd, Hf and Pb isotope ratios, xenoliths metasomatized by carbonatic-silicate melts show a stronger affinity with the EM-I component, while the one metasomatized by silicate melts are closer of the EM-II component. This suggests that the carbonatic-silicate and silicate melts do not initially originate from a homogeneous source that later separated due to immiscibility at shallow depths between silicate and carbonatic melts, but instead reflect the heterogeneity of the Kerguelen mantle plume.

Borosilicate glass alteration driven by magnesium carbonates
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Multi solid interactions: experiment and modeling
Geochemical modeling of glass and silicate mineral alteration is a major challenge for understanding natural processes in the earth sciences (e.g. chemical compositions of natural waters and oceans...). In confined media, solids reactivity quickly controls solution compositions. The alteration of a simplified synthetic glass, representative of the French reference nuclear glass in the presence of a simple Mg-bearing phase is a key step towards the understanding of the interactions between nuclear glass and nearfield materials in geological repository. Indeed, magnesium in solution is one of the elements known to potentially enhance glass alteration. In a first study, hydromagnesite was chosen as the simplest and as the most reactive Mg bearing carbonate.

Experiments were performed in closed system at 90°C and characterized by SEM, XRD and ToFSIMS. They revealed that glass alteration is enhanced in presence of hydromagnesite at 90°C.

Geochemical modeling was performed using the GRAAL model [1] implemented within the CHESS/HYTEC reactive transport code. The model was efficient enough for quantifying the amount of present solids, the pH and the elements concentration with time whatever the glass/hydromagnesite ratio.

Future experimental and modeling work will concern more representative solids, like dolomite and smectites.


Carbonation of forsterite and serpentine: Modeling the optimum conditions in terms of pH and temperature
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Carbonation of forsterite into magnesite and quartz following the reaction:

\[ \text{Mg}_2\text{SiO}_4 + 2\text{CO}_2 \rightarrow 2\text{MgCO}_3 + \text{SiO}_2 \]

has been assumed in a plethora of studies. However the consumption of metals by the formation of secondary phases has been overlooked.

In this study we intent to shed some light and define the conditions of successful carbonation experiments and industrial CO₂ mineralization projects in terms of pH and temperature. In order to minimize the precipitation of secondary phases we have mapped out the thermodynamic stability of magnesite relative to mineral phases like antigorite and brucite from 25 to 200°C, a pH ranging from 4 to 8 and 10 bars of CO₂ and performed both closed system batch simulations and kinetic simulation of the carbonation of forsterite and serpentine using the kinetics expressions and data available in the literature.

The results illustrate several important constrains on the formation of magnesite or serpentine. A key role in the reaction process is played by the temperature, due to the lowering reaction rates below 100°C where both magnesite and quartz fail to precipitate; whereas at temperatures greater than 200°C the overall forsterite to magnesite reaction is thermodynamically unstable. Furthermore, the pH effect cannot be ignored, as at pH below 4 the magnesite is extremely soluble and will not precipitate whereas at pH above 9 brucite is becoming the dominant precipitating phase, thus it is unlikely that carbonation will occur.
SIMS U-Pb ages for heterogenite from Katanga (DRC): Implications for the genesis of Co-U deposits in Shinkolobwe

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Heterogenite (CoOOH) deposits are the most abundant Co ore in the Katanga Copperbelt (DRCongo), which hosts world-class Co deposits accounting for ~50% of the world’s reserves [1]. Most of the heterogenite deposits occur in the upper oxidized zone of the primary deposits, and were formed during a Mio- Pliocene major uplift and weathering episode [1]. Most of the heterogenite deposits occur in the upper oxidized zone of the primary deposits, and were formed during a Mio- Pliocene major uplift and weathering episode [2]. However, U-rich heterogenite, present in deeper zones of several deposits, may have a different origin and age.

During a Mio-Pliocene major uplift and weathering episode [1], most of the heterogenite deposits occur in the upper oxidized zone of the primary deposits, and were formed during a Mio-Pliocene major uplift and weathering episode [2]. However, U-rich heterogenite, present in deeper zones of several deposits, may have a different origin and age.

Assuming that U in this heterogenite is in the UO2 form, we attempted to obtain in situ U-Pb ages for heterogenite samples from Shinkolobwe, using a Cameca IMS 1270 ion microprobe, with settings comparable to those used for standard U-Pb age measurements on uraninite. These analyses yield two distinct Neoproterozoic ages, recorded by the upper intercept of the concordia lines: 680.9 ± 7.4 Ma and 823.2 ± 2.2 Ma. In both cases, the lower intercepts provide imprecise zero ages, indicating recent (or continuous) Pb loss from the heterogenite.

At the present stage of knowledge, the 823 Ma date cannot easily be related to a known oxidizing event in the area. It is, however, reasonably close to the 816 ± 62 Ma Re-Os age obtained for Zambian primary sulfides [3]. The 681 Ma date could correspond to the Nguba karstification/weathering event [4]. If our age is meaningful, heterogenite could have formed in a period of superficial weathering, during the formation of the Katanga basin. This supergene event would, however, be contemporaneous with significant precipitation/reconcentration of uraninite, since the oldest uraninite age obtained for the Shinkolobwe deposits (at 652.3 ± 7.3 Ma) overlaps with ages for heterogenite in 207Pb/206Pb age density diagrams.

At this stage, the present study does not allow a full understanding of the timing and conditions of Co and U mineralization in Katanga. The results, however, indicate the importance of acquiring additional ages for heterogenite-uraninite deposits in order to understand the genesis of these giant Co-Cu-U ore deposits.


Chemical limits of trace elements in pyrite

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Pyrite in magmatic-hydrothermal settings contains significant concentrations of trace elements of economic and environmental importance, including Ag, As, Au, Bi, Cd, Co, Cu, Hg, Ni, Pb, Sb, Se, Te, Ti and Zn, which reflect the availability (solubility) of these elements in their parent hydrothermal solution. A review of our own and published analyses (including EMPA, SIMS, LA-ICP-MS, PIXE and HRTEM) of pyrite from Carlin-type, epithermal, and orogenic gold deposits reveals positive correlations for Sb-Pb-Bi, Au-Ag, and Cu-Ag-Sb in all samples. Element-element ratios for most analyzed pyrites are: Au/Ag – 0.8-1.1, Au/Te – 0.8 to 1.0, Ag/Sb – 0.7 to 1.1, Te/Pb – <1.1, Sh/Pb – 0.9-1.1, Sh/Cu – <1.0, Ag/Pb – 0.8-1.1, Bi/Pb – 1.0-0.7, and Bi/Sb – 0.7-1.1 in all types of deposits. Silver is enriched with respect to Te in low-T deposits, which have relatively high Ag/Te ratios of 1.0-1.2. Previous work has shown that As facilitates the incorporation of Au into pyrite via structural distortion and charge imbalance and that the Au content of pyrite is related to its As content such that the maximum Au content is CAu = 0.02CAs + 4·10^-5. Pyrite with Au-As contents above this maximum contain nano-inclusions of Au. These relations apply to epithermal and Carlin-type deposits, which form at relatively low temperatures. Au-As relations in pyrites from orogenic gold and skarn deposits, which form at higher temperatures, show similar relations but with smaller amounts of Au for any specific As content, suggesting that the solubility of Au in pyrite (as a function of As) decreases with increasing temperature. Arsenic also appears to facilitate incorporation of Ag, Te, Sb, Bi and Hg into the pyrite structure in the same mode as for gold, although analyses are not sufficient to establish specific solubility limits. Samples with contents of these elements that exceed the apparent solubility limits contain nanoparticulate sulfides and sulfosalts in distorted, polycrystalline areas of pyrite.

Mineralogical Magazine  www.minersoc.org
Boron isotope systematics during magma-carbonate interaction

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Carbonate assimilation is increasingly recognised as an important process affecting the compositional evolution of magma and its inherent ability to erupt explosively due to release of carbonate-derived CO₂ [e.g., 1, 2, 3]. In order to gain insights into this process, we performed short time-scale carbonate dissolution experiments in silicate melt using natural starting materials from Merapi and Vesuvius volcanoes at magmatic pressure and temperature [1, 4]. The experiments enable us to resolve in detail the timescales, textures and chemical features of carbonate assimilation. Three compositionally distinct glass domains have been defined: i) Ca-normal glass, similar in composition to the starting material; ii) Ca-rich, contaminated glass; and iii) a diffusional glass interface between the Ca-normal and Ca-rich glass. Here we present new boron isotope data for the experimental products obtained by SIMS. The glasses show distinct and systematic variation in their ¹¹B values. The contaminated regions generally show extremely negative ¹¹B values (down to -41 ‰) relative to fresh arc volcanics (-7 to +7 ‰ [5]). Considering that carbonates have ¹¹B values of +9 to +26 [6], the data can not be explained by simple mixing processes between the end-members alone. This implies that the ¹¹B of the original contaminant was drastically modified before being incorporated into the melt, which can be explained by B isotope fractionation during early degassing of the carbonate. Our preliminary results are the first of their kind and provide well constrained insights into the behaviour of boron upon degassing of carbonate. This in turn has implications for both late stage contamination in dangerous volcanic systems and deep subduction zone processes, where B is frequently employed as a tracer of crustal recycling.


Alteration of nitrogen isotopic signatures during phytoplankton degradation

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Stable nitrogen isotope ratios in sediments are widely used in paleoenvironmental studies to reconstruct past biogeochemical conditions and processes in the water column. Previous investigations have revealed that both the decay of sinking particulate organic matter in the water column and early diagenesis of deposited organic matter within sediments are associated with significant bulk N isotope effects that can mask primary isotope signals.

To study the mechanisms that underly the alteration of N isotope signals by bacterial degradation, we conducted a series of oxic and anoxic incubation experiments that mimic the decay of organic matter in nature. We used closed system experiments containing defined algae/sediment mixtures (Chlorella vulgaris), suspended in oxic or anoxic water from Lake Lugano, and inoculated with a natural consortia of bacteria. In order to assess N isotope partitioning during simulated organic matter decay, we monitored the N-isotope changes in specific organic (amino acids, amino sugars) and inorganic compounds (NH₄⁺, NO₃⁻) in both the particulate and dissolved fractions.

We will present initial data in the light of organic compound selectivity, kinetic isotope fractionation associated with degradation of specific organic components, and the effect of bacterial biosynthesis on bulk N isotope composition during early diagenesis.

Age and geochemical characteristics of the Malayer plutonic complex, West of Iran

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The Malayer plutonic rocks (48° 35'-48° 54' E and 34° 03'-34° 20' N) are located in Sanandaj-Sirjan zone. The plutonic rocks in this region were attributed to active continental margin, and subduction of Neotethys under Iranian micro-continent. Based on field observations and petrographic studies, this region can be divided into three major parts: Granitic, Granodioritic and Gabrodioritic. The isotopic studies have been shown that initial Sr ratios range from 0.70797 to 0.71087, eNd(t) from -2.3 to -4.9 and TDM from 955 to 1.33 Ga. The Rb/Sr and Sr isotopic ratios of the Malayer rocks are consistent with lower crust and oceanic sediments signatures. All felsic and intermediate samples regardless of their ages have a negative eNd(t) values and plot close together in eNd(t) vs Rb/Sr(i) diagram and mid-Proterozoic depleted-mantle model ages, which shows a genetic link between them. These isotopic signatures, coupled with the presence of inherited zircon with Proterozoic and Paleozoic ages, suggest that these rocks are the products of crustal melting and crust-mantle interaction during arc magmatism along the active margin of Iranian micro-continent in the Middle-Jurassic. U-Pb dating for this rocks yielded data between 162 Ma and 187 Ma (Middle-Jurassic). With respect to similar state in adjacent regions of MPC in SSZ, has been suggested that in Middle Jurassic had been occurred extreme plutonism. Based on different geochemical evidences such as discordant variation pattern for some major and trace elements between felsic to intermediate rocks and mafic rocks to enclaves and from mafic to felsic rocks, high potassium calc-alkaline character of granite rocks, enrichment of LILEs in comparison with HFSEs, constant variation of compatible elements such as V, Ni, and Cr in the differentiated phases, negative anomaly of Nb and Ta, and Eu negative anomaly, the main processes in formation of granite are magmatic differentiation associated with crustal contamination and with respect to equivalent age of granite and diorite that indicate the contemporaneity of the granite and basaltic magma, magma mingling or mixing for diorites and magmatic enclaves. Negative anomaly of Eu, non-concordant REEs variations, low enrichment of LREEs in mafic rocks imply to plagioclase differentiation due to partial melting process. These may indicate partial melting of ultramafic source as responsible for generating of mafic rocks.

Origin and isotope composition of the radium content in highly saline fluids

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The occurrence of highly saline fluids is characteristic for several facilities in deep geothermal energy. These brines contain inter alia enhanced contents of the radium isotopes 226Ra, 228Ra and 224Ra. Activity concentrations up to 50 Bq l⁻¹ were observed for geothermal systems in Germany. Radium isotopes are accumulated in scales of the Ba/SrSO₄ type resulting in specific activities > 500 Bq g⁻¹ [1]. Such levels of natural radioactivity demand for the application of radiation protection measures in the plant.

This phenomenon is not only limited to hydrothermal systems. Deep waters from rock aquifers can show salinities > 100 g·l⁻¹, thus enhanced geothermal system (EGS) plants may also be faced with this problem.

Otherwise, the concentrations and the isotope ratios of these three radium isotopes with quite different half-lives in the order of days until 10⁴ years allow conclusions about origin and transport characteristics of the geothermal brines.

A detailed investigation of the radium release at the rock/fluid interface is necessary for the description of the source term of radium isotopes in hydrothermal brines. The α-recoil during the decay of the thorium precursors in the decay chains (230Th → 226Ra, 232Th → 228Ra, 228Th → 224Ra) is considered as the dominating process in comparison to selective solution. Based on a range calculation for the recoil nuclei by the SRIM code [2], a model was developed that predicts the concentration of each radium isotope in the fluid. The crucial parameters according to this model are the U/Th-contents of the source material and its specific surface.

The model was tested on the well investigated aquifer system of the deep geothermal plant at Neustadt-Glewe, Germany. A good agreement between modelling and analytical results was obtained.

The radium concentration can be predicted for any aquifer type if its composition and structure are sufficiently known. Otherwise, the model may serve as a tool for clarifying the source of saline waters in hardrock systems.

Correlations between Hf, O and trace element concentrations in zircon from rhyolitic rocks (NE German Basin)

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Hundreds of deep hydrocarbon exploration wells exposed the Late Paleozoic volcanic province in NE Germany, which covers the area 500 by 800 km² and comprises rhyolites (ca. 70%), andesites and basalts (ca. 30%) [1]. SHRIMP zircon emplacement ages of volcanic rocks in NE Germany range from 303 to 290 Ma with the major peak of the volcanic activity being 299 - 295 Ma [2,3].

The range of \( ^{176}\text{Hf} \) and \( ^{18}\text{O} \) values in these magmatic zircons in the three sites investigated have been modelled by simple assimilation - fractional crystallization processes of mantle derived magma contaminated by sediments with model ages of ca. 2.1 Ga.

Trace element composition of zircons do not correlate with the isotopic composition, but zircons from the least contaminated sample have different chemical characteristic to that of zircons from more contaminated samples. For example distribution of Hf is bimodal in the least contaminated sample, whereas Hf has intermediate values in the more contaminated ones. The implication is that the least contaminated sample contains zircons from various sources recording different stages of fractional crystallization, whereas more contaminated samples contain one population of zircons, probably crystallized from the surrounding magma.

Acknowledgements: The study was funded by the grant Iuventus Plus from the Polish Ministry of Science to AP.


Melts in the deep mantle: Insights from first principles molecular dynamics

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As the primary medium through which planetary differentiation occurs, silicate melts are a key entity in the study of the thermal and chemical evolution of Earth. Over the past few years we have used first-principles molecular dynamics simulations to investigate the liquid state physics of the magnesio-, calio- and aluminosilicate melts at pressure and temperature conditions relevant to the entire mantle. First-principles methods characterize bonding directly in terms of the electronic charge density computed via density functional theory, and is equally robust at ambient and extreme pressure and temperature conditions. This allows accurate predictions of the physics of melts at extreme conditions to be made.

Liquid state diffusion and thermodynamics have been investigated in detail, with special attention to dependence on pressure, temperature and composition. Comparison to corresponding changes in liquid structure enables us to understand thermodynamic and diffusive behavior in a detailed atomistic context. Our results provide a rigorous test for a new fundamental thermodynamic relation for melts, which we derived to accurately describe liquid state thermodynamics. The relation is unique in that it accounts for electronic free energy contributions and displays the correct limiting behavior at extreme volume and temperature, capturing the thermodynamics of liquid-vapor coexistence.

Our work has allowed for deeper insight into the evolution of terrestrial planets, including the thermal state and mode of crystallization of magma oceans, the possible presence of melt in the deep earth, and their relative buoyancy. This insight in turn acts as a guide for questions to be addressed in the future, as first-principles simulations of systems of larger numbers of atoms and complex chemical compositions representative of natural systems become feasible.
Ab initio study on lattice thermal conductivity of minerals

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Thermal transport property of materials under pressure and temperature is of importance for understanding the dynamics of the solid Earth and the thermal history. However, both experimental and theoretical determinations of the thermal conductivity still remain technically challenging particularly at the deep mantle condition.

Recent progress in ab initio computational method based on the density functional theory (DFT) is making it possible to examine the transport phenomena including the lattice thermal conduction. The intrinsic bulk thermal conduction of insulator is essentially caused by lattice anharmonicity owing to phonon-phonon interaction. Determination of the anharmonic coupling constant is therefore the key to predicting the thermal transport property. Earlier theoretical works calculated the lattice thermal conductivity of MgO with ab initio molecular dynamics (MD) simulation or direct evaluation of the anharmonic force constants [1,2]. However, in these approaches, the simulation cell size could often be insufficient for accurate description of the long wavelength phonon scattering. As an alternative approach, the anharmonic coupling strength between phonon modes can be more efficiently and more accurately evaluated within the density functional perturbation theory (DFPT). In this approach, the higher-order force tensors are calculated based on the perturbative scheme taking care only of the primitive cell. We developed a technique for calculation of the phonon linewidth to obtain the phonon lifetime. Then the lattice thermal conductivity is evaluated combining with additional harmonic-level properties. In this presentation, we show the decay process of phonons and the lattice thermal conductivity of MgO and some typical minerals as a test for the applicability of our technique.

Research supported by Senior Research Fellow Center, Ehime University.


Modelling of long-term diffusion-reaction in the Callovo-Oxfordian clay for radioactive waste confinement

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One of the French options for the final disposal of high-level radioactive waste is a deep geological repository into the Callovo-Oxfordian formation (COX, Haute-Marne, Meuse, France). In this concept, COX clay associated with compacted bentonite, or not, may constitute the barrier system. In such systems, the interactions between groundwater and clays, as well as between the corrosion products of steel overpacks and clays under the influence of temperature elevation, may modify the chemical and physical properties of the selected clay buffers. Clay material has a low permeability, and consequently molecular diffusion is the main mechanism of mass transport in a clay barrier. The system is modeled in reducing conditions using the KIRMAT code (KInetic Reactions and MAss Transport). The software has been developed [1] from the single-reaction path model KINDIS [2] generated from the purely thermodynamic code DISSOL [3, 4].

This study is focused on the possible feedback effects of geochemical reactions on the transport properties (porosity and diffusion) of COX clay. The results of modeling obtained after 10,000 years of simulated mass transport-reaction are compared to the previous studies on an engineer pure bentonite barrier [5, 6, 7, 8, 9]. The mineralogical modifications of clays in contact with the geological interacting fluid, and with Fe2+ and OH- ions provided by the corrosion of the steel overpacks as well as the evolution of porosity and molecular diffusion will be discussed.

Mediterranean sapropel formation; Preservation and palaeoceanography

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Precession-related deposition of eastern Mediterranean sapropels are associated with humid climate conditions. The last of such 'humid periods' occurred from 10.4 to 5.7 kyr 14C ago, simultaneous with the sustained wet period in the circum Mediterranean area. The end of this humid period coincides with a high peak of MnO2. This peak in all 30 studied cores occurs in response to a relatively abrupt re-ventilation event at 5.7 kyr. Subsequently, oxygen continued to progressively move downward into the sapropel sediment thus removing organic C and organic biomarkers. Such removal mechanism seriously affects the traditional interpretation based on palaeoproxies.

From a detailed study of the mechanisms of formation of sapropel S1 across the eastern Mediterranean basin as a function of time and water depth, we demonstrate that surface waters had a reduced salinity and concomitantly that the deep (> 1.8 km) eastern Mediterranean Sea was devoid of oxygen during 4,000 years of S1 formation. This has resulted in a differential basin-wide preservation of S1 determined by water depth, as a result of different ventilation/climate-related redox conditions above and below 1.8 km. Climate-induced stratification of the ocean may thus contribute to enhanced preservation of organic matter, ie to formation of sapropels (and potentially black shales).

Production flux of sea-spray aerosol

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Knowledge of the size- and composition-dependent production flux of primary sea-spray aerosol (SSA) particles and its dependence on environmental variables is required for modeling cloud microphysical properties and aerosol radiative influences, interpreting measurements of particulate matter in coastal areas and its relation to air quality, and evaluating rates of uptake and reactions of gases in sea-spray drops. The current status of the knowledge on the primary SSA production flux, mainly for particles with \( r_{eq} \) (equilibrium radius at 80% relative humidity) less than 1 µm, has recently been reviewed by de Leeuw et al. (2011). These authors discussed the production of sea-spray particles and its dependence on controlling factors which have been investigated in laboratory studies that have examined the dependences on water temperature, salinity, and the presence of organics, and in field measurements with micrometeorological techniques that use newly developed fast optical particle sizers. Extensive measurements show that water-insoluble organic matter contributes substantially to the composition of SSA particles with \( r_{eq} < 0.25 \) µm and in locations with high biological activity can be the dominant constituent. Order-of-magnitude variation remains in estimates of the size-dependent production flux per white area, the quantity central to formulations of the production flux based on the whitecap method. This variation indicates that the production flux may depend on quantities, such as the volume flux of air bubbles to the surface, that are not accounted for in current models. Variation in estimates of the whitecap fraction as a function of wind speed contributes additional, comparable uncertainty to production flux estimates.

de Leeuw et al. (2011) conclude that despite the many gains in understanding in recent years, the uncertainty in the SSA production flux remains sufficiently great that present knowledge of this quantity cannot usefully constrain the representation of emissions of SSA in chemical transport models or climate models that include aerosols. As a consequence it is not yet possible to improve the modeling of these emissions much beyond the current state of affairs which shows nearly two orders of magnitude spread in current estimates of global annual SSA emissions.
On the morphology and chemistry of (micro)fossils: Matches, mismatches and kerogen formation

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The far greater part of organic matter on Earth is present in sediments and consists of high molecular weight, insoluble constituents collectively known as kerogen. To improve our understanding of the origin, chemistry and fate of this kerogen, morphologically well preserved organic (micro)fossils and their extant counterparts are studied assuming that the preservation of such fossils is a consequence of the resistance towards (bio)degradation of the organic constituents they are made of.

Many investigations of well-preserved (micro)fossils and laboratory experiments with their extant counterparts using pyrolytic, chemical and spectroscopic analytical approaches do indeed indicate that biopolymers such as algaenan in algae, cutan in plant cuticles and lignin in wood are resistant towards diagenesis and may thus be responsible for excellent fossil preservation.

However, this “match” of preserved biochemistry and morphology is not always encountered. In many well-preserved fossil algal cells and plant cuticles and their extant counterparts these resistant biomacromolecules, algaenan and cutan resp., are completely absent. Recent studies seem to indicate that the excellent preservation of such fossils is due to a gradual replacement of originally present labile bio(macro)molecules by newly formed highly resistant geomacromolecules without significant morphological changes, a “mismatch” between biochemistry and morphology. In particular studies of sporopollenin in extant and fossil macro- and microspores indicate that pre- or post depositional exposure of organic entities to oxygen triggers oxidative cross linking of “nearby” low molecular weight (poly)unsaturated membrane lipids resulting in resistant, mainly aliphatic geopolymers partly or completely replacing the original biopolymers.

This kind of (micro)fossil studies is crucial to unravel the molecular structure of kerogen and, consequently, to understand the molecular chemistry of fossil fuel genesis.

Origin of karstic dissolution voids in Jurassic shallow marine carbonates at SW of Ankara, (Turkey)

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Jurassic rocks cropping out at the southwest of Ankara (Turkey) rest unconformably on the basement rocks commonly as microbial deposits but also as detrital sediments. Karstification occurs in shallow marine biomicrite bearing sponge spicules as well as in microbial carbonates. Most of the cavities in the carbonates developed when they were carried to subaerial conditions as a result of sea level changes and, also by tectonic activities. Karstic voids are irregular in shape and disconnected. Their fillings are initiated with more than one crystallization phase of low-magnesian calcite with different colors [1]. Following this coating crystallization phase, the remaining voids were filled by different type of sediments. These infilling sediments are generally laminated, pink, or in different color.

They are vadose silts in varying size, but in some cases, comprises grains derived from host rocks. Compared to others, some karstic cavities are large. They were interpreted as being formed following fracturings in relation with tectonic activities. These cavities commonly were filled by marine sediments. Being coated by calcite crystals implies that these cavities were inundated by marine water having adequate condition for calcite crystallization before filling by marine sediments. Lamination of fine filling sediments is commonly parallel to the parent rocks. But fillings of cavities in a 12 cm thick layer have laminated sets which are neither parallel to each other nor to the bedding of parent rocks. This shows that the basement of the basin was not stable and, was tilted differently in time.

Potentiality and limits of applying DSC and TG to complex systems:
Direct and indirect information

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The relationships between agriculture and environmental quality find a key issue in the study of the processes enhancing organic matter stability in soil, in order to increase C sink and mitigate the effects of global change. Various and different approaches are possible, due to the complexity and heterogeneity of the soil system where SOM chemical composition and its architecture are widely interdependent within the soil matrix. In recent years the application of thermal analysis to the study of soil organic matter has found a renewed interest, mainly due to the possibility to obtain quantitative estimation of organic matter within the soil mineral matrix, possibly without chemical extraction. In addition, the dynamic measure conditions obtained through the thermal scans give the theoretical possibility to deduce the kinetics of the thermally induced processes. Different patterns of thermal stability are shown by different biomasses, compost or soils. However, it could be misleading to assimilate the time based output of DSC and TG measures to the kinetics of the processes occurring in soil, thus the concepts of organic matter stability or lability or recalcitrance needs to be better defined according to appropriate definition of the reference context.

In the presentation, the comparison between information obtainable from compost or soil analysis will help us to highlight potentiality and limits in applying DSC and TG to complex systems in order to move from a qualitative approach to a better definition of thermal and biochemical stability indexes. Finally, an open question should be discussed: can we forecast or imagine to include information on thermal behaviour of SOM within an ecological approach to the soil system?

Sorption of metals on a novel synthesized Mn (oxy)hydroxide

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Novel synthetic manganese (oxy)hydroxide

A novel synthetic manganese (oxy)hydroxide is synthetized using the modified protocol of Ching et al. [1], which is commonly used for the preparation of birnessite. This (oxy)hydroxide is studied as a possible chemical stabilizing agent for metals in contaminated soils. Its stability in deionized water and the sorption of Cu and Pb are studied.

Figure 1: Adsorption isotherms of Cu and Pb on the Mn (oxy)hydroxide at pH 4

Results

The dissolution of the Mn (oxy)hydroxide in water reaches 12 and 1 mmol/g for solid/liquid ratios of 1/500 and 1/10, respectively and indicates that the phase could be fairly stable in soils. The Langmuir isotherm parameters calculated show that the maximum adsorbed quantity of Cu and Pb reach 1.3 and 0.6 mmol/g. The sorption parameters of the Mn (oxy)hydroxide were compared to those of birnessite at pH 4, which reached 1.1 and 1.4 mmol/g for Cu and Pb, respectively. Birnessite thus adsorb better Pb than the synthesized phase, but for practical use as a chemical stabilizant, our Mn (oxy)hydroxide could be promising due to its easy synthetisation.

Impact of authigenic particles on phosphate and trace metal budgets of anoxic basins

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Intense element cycling causes steep gradient of nutrients and redox-sensitive trace metals at pelagic redoxclines; the transition zone separating oxygenated surface waters from sulphidic bottom waters. Besides well-known Mn-oxides, SEM-EDX inspection of authigenic particles from the redoxcline of the Black and Baltic Seas evidence existence of postulated Fe-phosphates as well as mixed phases comprising Mn, Fe, and P as a new solid species (Mn-Fe-P shuttle). Throughout the redoxcline, these minerals show a general succession with maximum abundance of Mn-oxides above the redoxcline followed by mixed phases and almost pure Fe-phosphates within and below the redoxcline. Morphological similarities and molar Fe/P ratios suggest the formation of irregular Fe-oxyhydroxo coatings on sinking MnOx particles followed by immediate adsorption of phosphate. Despite oxidation by O2, batch-type experiments using biogenic Mn-oxides demonstrate the efficient potential of Fe3+ oxidation by sinking MnOx particles. When entering sulfidic waters MnOx is further reduced, thus causing an increasing relative abundance of Fe-phosphate. We suggest a conceptual model for the Mn-Fe-P shuttle at pelagic redoxclines, which affects phosphate transport throughout the water column and thus impacts primary production at least over longer time scales. This Mn-Fe-P-shuttle likely played an important role for the cycling of P in ancient ocean basins, e.g., during certain periods of Cretaceous black shale formation and should be considered in future modelling approaches dealing with stratified ecosystems. Furthermore, this shuttle influences the cycles of certain trace metals via scavenging. High-resolution determination of trace metals in sapropelic sediments from the Gotland Basin (Baltic Sea) will be compared with the elemental composition of authigenic particles from the water column in order to assess preferential enrichments in the sedimentary record.

Li content and isotopic distributions in granulate of Kerguelen plateau

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Kerguelen basalts contain abundant mantle xenoliths, including mantle peridotites and deep magmatic segregates equilibrated in the granulate facies [1]. Lithium chemical and isotopic distribution were measured in two pyroxene granulites, in order to define their signature and describe the Li behavior during the lower crust formation processes. Li content and isotopic composition were measured in using the Cameca IMS 1270 Ion probe at CRPG, with reference Cpx and Opx with compositions close from those of the samples. The studied xenoliths display close mineralogical compositions, bearing Mg81-92 Al-diopside, Mg78-93 enstatite and labradorite or bytownite. Spinel and garnet are observed in 2 of them, and they all are type II xenoliths [1,2]. On the whole rock scale the Li contents range from 1.5 up to 9 ppm, with Li content decreasing from Cpx to Opx with a ratio Opx/Cpx of 0.8-0.9 and a ratio Plag/Cpx of 0.2-1. At the grain scale, Li displays a homogeneous distribution, at the exception of depleted or enriched Cpx rims. Only the more Li depleted sample display heterogeneous Li distribution in both Cpx and Opx.

The δ7Li values measured on Cpx and Opx range between +4 and +14, with most of the values between +5 and +8. The Cpx depleted or enriched rims display δ7Li values associated to Li diffusion. Only the Li poor xenolith display δ7Li values scattered on a large range, from -9 to +14. A general observation is that Cpx display rather slightly higher δ7Li values than Opx, and those values are more scattered in Opx than in Cpx. The δ7Li values for Plag are in progress and will be presented, but could not affect a lot the Li isotope budget, are most of Li is beard by Opx and Cpx.

The bulk value for these granulite samples is in agreement with a direct derivation from the mantle (5-8 ppm, δ7Li=-5). But their Li content is lower than expected for the lower continental crust [3], suggesting that Li in the lower continental crust is not mainly derived from the mantle.

Contrasting silicon and magnesium isotope fractionation with clay mineralogy in volcanic soil weathering sequences, Guadeloupe

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The weathering of continental silicate rocks influences global climate by consuming atmospheric CO₂. Magnesium and Si stable isotopes are used as weathering proxies in soils and rivers, but the impact of the mineralogy of secondary phases on isotope fractionation remains unexplored so far. Here, we investigate variations in $^{26}\text{Mg}$ vs. DSM-3 and $^{30}\text{Si}$ vs. NBS28 in bulk soils and clay fractions relative to their parental andesite in two soil weathering sequences (Guadeloupe) that were formed in contrasting climatic conditions. The Western slope of La Soufrière volcano (dry conditions) presents a soil sequence Andosol - Cambisol - Vertisol with formation of smectite, whereas the Eastern slope (high rainfall) presents Andosol - Nitisol - Ferralsol with formation of kaolinite.

For Mg isotopes, clay fractions ($\delta^{26}\text{Mg} -0.41$ to $-0.10\%e$) were isotopically heavier than the andesite ($\delta^{26}\text{Mg} -0.47\%e$), supporting a preferential incorporation of heavy Mg isotopes in secondary Mg-bearing clay minerals. The clay fractions on the Eastern slope were progressively heavier with increasing weathering degree, -in contrast to the Western slope were clay fractions were progressively lighter with increasing weathering degree and with increasing exchangeable Mg associated with smectite. For Si isotopes, clay fractions were lighter than the parental material, and progressively lighter with increasing weathering degree. More importantly, larger Si isotope fractionation was associated with the formation of kaolinite ($\delta^{30}\text{Si} -1.95$ to $-1.32\%e$) than with the formation of smectite ($\delta^{30}\text{Si} -1.05$ to $-0.94\%e$) relative to the parental andesite ($\delta^{30}\text{Si} -0.37\%e$). Our results highlight that a similar parental andesite exposed to different climatic conditions can generate contrasting Mg and Si isotope fractionations in secondary phases, which offers great potential for paleo-reconstruction of soil environments.

Impact of reductants on the optical properties of Humic Substances (HS)

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Our previous results have shown that the reduction with sodium borohydride of Suwannee River humic and fulvic acids, a commercial lignin, and a series of solid phase C18 extracts from fresh, estuarine, coastal and offshore waters of the middle Atlantic bight produces a preferential loss of long wavelength (visible) absorption and enhanced, blue-shifted emission [1]. These results are consistent with and interpreted within a previously proposed charge transfer model [2, 3]. Here we extend this work to other reducing agents (such as cyanoborohydride and sodium dithionite) and other humic substances (from aquatic and soil environments) to investigate the impact of other reductants on the optical properties of humic substances and attempt to assess the relative importance of quinones and ketones to the optical properties of these materials. Preliminary results indicate that a) borohydride reduces all HS examined independent of their source as determined by UV/Vis and fluorescence; b) cyanoborohydride did not reduce any of the HS examined to a significant extent; c) dithionite appears to reduce HS but to a much smaller extent that borohydride. Ongoing work aims to extend this work to more HS and model quinones/ketones and to quantify the loss of absorption with respect to dithionite consumed.


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δ³⁰Si and Ge/Si changes in BIFs along the Archaean
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The Precambrian ocean underwent a long-term cooling as inferred by oxygen isotopes and recently corroborated by an increase in δ³⁰Si values [1]. However, this was questioned because both primary and secondary cherts were considered. To get new insights to the Archaean ocean evolution, we coupled δ³⁰Si and Ge/Si ratios in Banded Iron Formations (BIFs) spanning a large time scale (from 3.8 to 2.46Ga). Trends in Si-rich mesobands of BIFs confirm an increase of δ³⁰Si values from ~-2.1‰ (3.8Ga, [2]) to ~-1.1‰ (2.46Ga) with a simultaneous decrease in Ge/Si ratios from ~29.1µmol/mol (3.8Ga, [3]) to 2.7µmol/mol (2.46Ga). We suggest they both reflect a decrease of high-T hydrothermal inputs to oceans through time. As high-T hydrothermal fluids display high Ge/Si ratios, a decrease in hydrothermal inputs would lower the oceanic Ge/Si ratio as well as it would have contributed to cool the ocean. The maintenance of an Early Archaean high-T ocean would prevent significant direct silica precipitation from the ocean and its gradual cooling would have facilitated direct silica-rich precipitation that may have led the oceans towards heavier δ³⁰Si signatures.


A warming-cooling cycle between 3.8 and 3.2 ky BP: Correlations of speleothem and bivalve compositions with ice core records
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Climate conditions during the Holocene were relatively stable compared to the entire Quaternary, so that only minor fluctuations are detectable – for example – in the stable isotope records of ice cores. On the other hand, climate fluctuation events have been detected in Europe by geological and geochemical records interpreted to reflect temperature and/or humidity changes, sometimes in contradiction with each other. In this study freshwater bivalve shells (Unio sp.) were collected from Bronze age archaeological excavations around Lake Balaton (Central-Western Hungary) spanning the period of about 3 to 4 ky BP and their stable C and O isotope compositions were measured in order to investigate lake evolution processes in this period of time. The data indicate warmer/dryer conditions around 3.7 ky BP, bracketed by relatively cooler and/or wetter environments. These observations seemed to be in contradiction with earlier results that lead us to compare the geochemical data from bivalve shells with speleothem records of the region as well as with the GISP2 ice core oxygen isotope data. H, C and O isotope compositions and trace element data (e.g., Mg/Sr ratios, P concentrations) in stalagmites can be correlated with the bivalve shell data, indicating warming around 3.8-3.6 ky BP associated with lower humidity during summer (elevated winter/summer precipitation ratio), followed by an ~300 year long cool phase with summer-dominated precipitation. Good agreements between different paleoclimate records indicate that the warming-cooling events affected a large region from the North Atlantic at least to Central Europe. Temperature and humidity variations inferred from the data suggest that the North Atlantic Oscillation was a major governing factor in climate changes during the Bronze Age.
Structure and relative stability of hydrous and anhydrous Ca-Mg carbonates from first-principle calculations

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Calcium and magnesium carbonates play an important role in the chemistry of the hydrosphere, lithosphere, atmosphere and biosphere. From a technological point of view, the precipitation of carbonates in industrial and domestic environments represents a problem in terms of process efficiency and maintenance costs.

The crystallisation and growth mechanisms of these compounds, as well as their structure and relative stability, are still a matter for investigation. In particular, relatively little data is available for the hydrated phases, due to limited natural occurrence and low stability. However, they may well play a role during the crystallisation and growth mechanism of the anhydrous phases (included Ca-Mg carbonate solid solutions) and in CO₂ sequestration, especially at low temperature [1-5]. Information regarding the formation of mixed calcium-magnesium carbonates is also pertinent to understanding the dolomite problem.

A comprehensive ab initio structural and thermodynamic study of calcium-magnesium carbonates and their hydrates will be presented. The good agreement between calculated and available experimental data attests to the validity of the applied computational approaches, namely Density Functional Theory in the present study.


Nucleation of amorphous calcium carbonate: A combined theoretical and experimental perspective

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The nature of the nucleation of amorphous calcium carbonate is examined in the light of both recent experimental [1,2] and theoretical [3] results. While experiment demonstrates the existence of stable pre-nucleation clusters, followed by a nucleation event, computer simulations suggest that the free energy of adding ion pairs to amorphous calcium carbonate is exothermic regardless of size, which may indicate the absence of a barrier. How these two different sets of observations can be reconciled will be examined in this work through the use of molecular dynamics simulations of pre-nucleation calcium carbonate solutions.

In this presentation we will explore the use of computer simulation methods to try to unravel the complexities of the nucleation and growth processes for calcium carbonate. Central to this is the development of a force field that is accurately calibrated against experimental free energies [3] since failure to do so can result in qualitative errors for interfacial properties. Based on this we have explored the stability of ACC versus crystalline nanoparticles while accounting for the variable water content in the amorphous structure [4]. In the light of this, and new experimental results, we propose a model to explain the non-classical aspects of the nucleation mechanisms of calcium carbonate, the origins for which can be traced back to the interfacial properties.

S in CAMP and Paraná-Etendeka CFBs

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Synchrony of continental flood basalts (CFB) and significant Phanerozoic mass extinction events may suggest a trigger effect of large scale basaltic eruptions on the global climate and environment, mainly due to intense emissions of volcanic gases such as SO2 and CO2 [1]. However, this interpretation is based on poorly constrained gas contents of the basalts and on even less well known gas emission rates. Here we investigate the S content of basalts of two of the largest CFB provinces: the Central Atlantic magmatic province (CAMP) and the Paraná-Etendeka (PE). Notably, while the CAMP is synchronous with and possibly triggered the end-Triassic extinction [2], PE basalts had a very minor effect on the early Cretaceous biosphere [3].

Melt inclusions in CAMP basalt olivines yield S contents (electron microprobe analyses) comparable to those found in Deccan basalts [1], whereas S in matrix glass is close to detection limit, suggesting that degassing during the eruption was almost complete.

As an alternative approach, we measure S (and Cl) contents (synchrotrone analyses) also in phenocrysts from CAMP and PE basalts and extrapolate the magmatic S content through newly established crystal/melt partition coefficients. These results illuminate the difference which seem to exist between the two CFB provinces and contribute to our understanding of their different environmental impacts.


Mineral chemistry and fluid inclusion characteristics of the Kabadüz Ore Veins (Ordu, NE-Turkey)

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Hydrothermal vein type deposits of Kabadüz region (Ordu, NE-Turkey), are located in the Upper Cretaceous andesitic-basaltic rocks and formed in fault zones of the NW-SE directions. The primary mineral paragenesis of the ore veins are composed of pyrite, chalcopyrite, sphalerite, galena and tetrhedrite-tennantite with quartz and lesser amount calcite and barite as a gangue mineral. Petrographical studies suggest that ore veins in the region have similar mineral paragenesis, succession and textural properties.

Pyrite contains up to 0.95 wt% Zn, and 0.60 wt% As, chalcopyrite contains up to 0.86 wt% Zn and 0.14 wt% Au. Sphalerite is poor in Fe and contains up to 0.35 wt% Mn, 2.18 wt% Cu, and 0.89 wt% Cd. Tetrhedrite and tennantite are also poor in Fe content (up to 1.56 wt%). Different phases from the each different veins are found to be similar in composition. Lower Ni and Co content of the pyrites and Zn/Cd ratio of the sphalerites suggest that hydrothermal solutions related to the acidic type magmatic activity.

Homogenisation temperature (Th) and salinity data vary between 180-436.1 °C and, 0.4-14.7 % NaCl, at the fluid inclusions of sphalerite and quartz. On the basis of first melting temperatures, CaCl2, MgCl2 and FeCl2 were dominant at the higher Th, whereas NaCl and KCl at the lower Th conditions. Salinity content of the inclusions imply that hydrothermal solutions related to the magmatic sources. On the other hand well defined positive correlation between Th and salinity indicate that meteoric water involved in the hydrothermal solutions. In addition to petrographical studies, mineral chemistry analyses and fluid inclusion properties indicate that ore veins in the region have occured same or similar ore formation conditions.
Water weakening in dunite: Highlights from torsion experiments

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We have performed torsional deformation experiments on pre-hydrogenated fine-grain olivine aggregates using an innovative assembly to estimate water-weakening in mantle rocks at high shear strains. San Carlos olivine powder was cold-pressed, then 45 µL of water was added, and the sample was subsequently hot-pressed at 1523 K and 300 MPa for 3 h, producing aggregates with average grain sizes of 7 or 15 microns. Deformation experiments were performed in a high-resolution gas-medium apparatus equipped with a torsional actuator under a confining pressure of 300 MPa, a temperature of 1473 K, and constant shear strain rates of 1.4 x 10^-4 to 8 x 10^-5 s^-1.

Peak shear stresses ranged from 150 MPa to 195 MPa, values slightly weaker than determined in previous torsion experiments on dry fine-grain dunites with equivalent grain sizes, shear strain rates, and finite strains. Textures and microstructures of the starting material and deformed specimens were fully characterized by scanning electron microscopy and by electron backscatter diffraction. All deformed aggregates show a shape preferred orientation marking a foliation and lineation, grain size reduction, and a well-developed olivine crystal preferred orientation consistent with deformation by dislocation creep with dominant activation of the (010)[100] slip system. The hydrogen concentration in olivine aggregates was determined with unpolarized Fourier transform infrared spectroscopy. Analyses of the spectra indicate that the hydrogen concentration of the olivine might be limited and show a potential contamination by water-rich inclusion or intergranular material. These torsion experiments on hydrogenated fine-grain dunite provide new insights into the water weakening phenomenon observed in various nominally anhydrous minerals.

A missing process in the Eastern margin of Tibetan Plateau from multi-system thermochronology and its implication for late Cretaceous tectonic change from the Paleo-Tethyan to Neo-Tethyan regime

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Due to lack of structural and sedimentary records to constrain the Jurassic-to-Cretaceous evolution, a missing process was here in Eastern margin of Tibetan Plateau. Given that all radioisotopic systems are subject to disturbance and resetting at different temperatures, we can restore the cooling process or emplacement of rock using different minerals or radioisotopic systems, which we call multi-system thermochronology. Based on the analysis of 125 thermochronology ages (e.g., U/Pb, Ar/Ar, Rb/Sr, FT, U-Th/He) of igneous rocks from the eastern margin of Tibet in the Yidun Arc, Yadjiang Depression and Songpan-Garze Fold Belt, we reconstruct the emplacement process of different granites using the multisystem thermochronology approach, to decipher the process.

At mid-to-late Indosinian, the initial emplacement age and depth of granites distinctly decrease from north to south, followed by a long slow cooling process in mid-to-upper crust during Yanshanian indicating a long period of thermal stability and tectonic quiescence. Those reflect the control of Paleotethyan tectonic setting. Whereas, between early and late Cretaceous, there was widespread granite emplacement and uplift-related cooling on the eastern margin of Tibet again, with the declining tendency of magmatic activity and tectogenesis from south to north due to far-field effects of Lhasa-Qiangtang collision. In addition, the granites in north do not have an obvious emplacement process. Which reflect the control of Neotethyan tectonic setting. Correspondingly, as a sedimentary response to the change of tectonic regime, there is an obvious change on depositional contact in adjacent basins from Late Cretaceous to Neogene. That is from a southward decreasing angularity of the unconformity in early to a northward decreasing angularity in later. Thus, the eastern margin of Tibet is thought to have experienced an important late Cretaceous (about 100Ma) tectonic change from the Paleo-Tethyan regime to Neo-Tethyan regime.
Effect of Carbon, Sulfur and Silicon on Iron melting at high pressure: Implications for composition and evolution of the terrestrial planet cores

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High-pressure Fe-S-C and Fe-S-Si-C melting experiments, with a reasonable abundance of carbon, sulfur and silicon in the terrestrial planet cores, have been conducted to investigate how melting relations and crystalization sequences change with pressure and bulk composition. The results were used to understand the composition and evolution of the terrestrial planet cores.

For Fe44.40C4.35S7.35, the first crystallized phase is Fe,C at 5 GPa and Fe2C at 10-20 GPa. For Fe43.10C10.85S11.41, Fe,C is the stable carbide at subsolidus temperature at 5-15 GPa. For Fe55.30C20.85S11.41 and Fe53.71C13.31S11.40, the first crystallized phase is metallic Fe instead of iron carbide at 5-10 GPa. It is observed that the coticetic curve between Fe and Fe,C moves toward the iron-rich direction with pressure increasing from 5 to 10 GPa in the Fe-C-S system. If this tendency persists to the Earth’s present pressure condition, only a small amount of carbon is needed to form an iron carbide solid inner core.

Experiments on Fe52.89C10.66S13.7Si2.89 show even a small amount of C significantly lowers the closure pressure of the miscibility gap. Given an Earth’s core containing a significant amount of S and moderate Si and with small amount of C, no compositional stratification is expected for Earth’s Fe-S-C-Si core, although it may occur during early melting events. It is observed that S preferentially partitions into molten iron while significant amount of Si enters the solid phase with temperature decrease. Meanwhile, the C concentration in the liquid and solid iron metal changes little with temperature variations. If Si, C and S partition behaviour between molten iron and solid iron metal with temperature are expected to be the same under Earth’s present core pressure condition, the solid inner core should be iron dominated with dissolved Si. On the other hand, the liquid outer core will be S rich and Si poor. Moderate carbon will be evenly present in both solid and liquid iron metallic core.

Based on our melting data in a multi-component system, no layered liquid core should exist in Venus and Mars, because of their high core pressures. On the other hand, Mercury, which has an estimated CMB pressure of ~7 GPa, may have a layered liquid outer core due to immiscible liquids (one is S rich and one is Si rich) and a solid Fe-Si inner core.
Confocal Raman spectroscopic characteristic of pseudoleucite in alkaline intrusive rocks: Central Anatolia, Turkey

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Pseudoleucite is one of the main mineral of the silica undersaturated rocks of alkaline rocks of Central Anatolian Crystalline Complex. The pseudoleucite comprises aggregates of K-feldspar and nepheline preserving orginal crystal forms of leucite. Confocal Raman spectroscopic studies reveal that the leucite has been replaced by disordered K-feldspar with a structural state intermediate between orthoclase and nepheline form in spheluritic texture under the microscope (Figure 1). The pseudoleucites are inferred to have grown of crystallization of leucite at high temperature and pressure then transformed to orthoclase with less amount of nepheline through reaction with sodium-rich fluids and PH$_2$O at low pressure and temperature in proportion to previous original formation of the leucite in the same system.

Figure 1: Macro (a) and micro (b-c) photographs of pseudoleucite and CR Spectrums of orthoclase and nepheline

Discussion and Results

Compositional zoning in primary and late-stage minerals indicates complex, multi-stage crystallization and replacement histories. Late stage fluids of alkaline magma, rich in F, Cl, CO$_2$ and H$_2$O, reacted with primary minerals to form complex intergrowths of minerals such as pseudoleucite, cancrinite, fluorite, V-bearing magnetite, F-bearing garnet and Na-augite. Early crystallization of apatite and titanite controlled the compatible behavior of P and Ti, respectively.

The formation of melanite and uvarovite garnet also affected the behavior of Ti, Cr as well as Zr, Hf and the heavy rare-earth elements in these rocks. The innovator crystalization of leucite, cause to intergrowths of K-feldspar and nepheline at the late stage of fractionation.

Global assessments of linkages between air quality and climate

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Aerosols are among the most important contributors to air quality problems, and are also active constituents of the climate system. Unfortunately, there are large scale differences between global climate models and urban-to-regional scale air quality models, which prevented consistent and extensive scientific analysis of air quality and climate impacts. In addition, since air pollution and greenhouse gas mitigation policies were often developed independently, a policy driver to integrate these urban-to-global scales was missing. This situation is changing- global models are increasing resolution, and regional models are expanding model domains. Global model analysis are used for air quality analysis, and regional models are use for regional climate assessments. The co-benefits for air quality are increasingly important aspects of climate policies, while targetted air quality policies may help to prevent rapid climate change on the decadal time scales.

In this overview talk, I will present results from the international HTAP (Hemispheric Transport of Air Pollution) assessment, with a focus on the role of continental transport versus ‘local’ emissions of aerosols and precursors, discuss re-analysis efforts to understand the interaction between changing climate and air quality in the past decades, and describe the current understanding of the health and climate effects of these aerosols on the global scale. I further present the implications and insights derived from various air pollution/climate scenarios resulting from recent assessments (GEA, RCP, etc).
Influence of solute-solvent interactions on mass discrimination during chemical diffusion

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Chemical diffusion in molten silicates and aqueous solutions leads to stable isotope variations in nature because chemical diffusivities are mass dependent. For diffusion in liquids, there is no general theory that relates cation diffusivity to mass, but mass discrimination during diffusion must be affected by the nature of cation-solvent interactions.

To investigate the relationship between liquid structure and cation diffusion, we measured Ca and Mg isotope diffusivities in silicate liquids using diffusion couples of natural and synthetic compositions. In all experiments, the initial isotopic composition is uniform and each isotope diffuses in the same direction down a substantial concentration gradient, enriching the Ca- or Mg-poor liquids in the lighter isotope by an amount dependent on: (1) the initial concentration contrast between liquids, (2) the relative chemical diffusivities of isotopes, and (3) the efficiency of isotopic exchange or self diffusion superimposed on chemical diffusion. Results from these experiments, in combination with results from natural volcanic liquids, show clearly that the efficiency of isotope separation ($E$) is systematically related to the solvent-normalized diffusivity - the ratio of the diffusivity of the cation ($D_{cation}$) to the diffusivity of silicon ($D_{Si}$).

We present an idealized quantitative model to explain the relationship between $E$ and $D_{cation}/D_{Si}$. The model views cation diffusion as a combination of two (or possibly more) distinct mechanisms of transport: “free” cations that site-hop among aluminosilicate structures, and “bound” cations that translate or rotate with aluminosilicate structures in the melt. We assume that the rate of exchange between free and bound cations is infinitely fast to maintain local equilibrium. In this model, the observed or net diffusivity and its mass dependence are determined by the relative abundance ($K$) of free versus bound cations in the liquid. This conceptualization provides a framework for describing mass discrimination in complex liquid systems and for understanding the role of diffusion in contributing to stable isotope variations in minerals.

Bimodal volcanism of the Northern frames of the Eastern link of the Mongolian-Okhotsk orogenic belt (Russia)

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In the Southern frames of Eastern link of Mongol-Okhotsk orogenic belt (MOOB), in the end of early Cretaceous (119 - 97 Ma), a bimodal volcano-plutonic complex was formed. It correlated by a whole number of parameters with bimodal formations of the Western link of the belt [1]. The formations in the Northern frames of the Eastern link of MOOB, that are analogical by the age and petrochemical characteristics, are separated. There are insignificant differences in geochemical characteristics (Fig.1). There are also diversities by isotopic parameters 87Sr/86Sr =0.70592-0.70620, by εNd(1) = (-11.77) – (-12.20) and TNd(DM-2st)=1901-1937 Ma [2]. Along Southern and Northern borders of the Eastern flank of MOOB the bimodal volcano-plutonic complexes were formed during 119-97 Ma. Their geochemical characteristics show that they were formed in the situation of convergence borders of the platforms (collision of North-Asian and North-Chinese continents).

Figure 1: Geochemical characteristics of the rocks of the bimodal complexes framing MOOB: 1 – Northern, 2 – Southern. Concentrations of the rear elements in the Compositions of chondrite C1 and primitive mantel are brought according to the data (Sun, McDonough, 1989).

The insoluble organic matter in carbonaceous meteorites

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Carbonaceous meteorites are the most primitive objects of the solar system. They exhibit significant carbon contents mostly occurring as insoluble organic matter (IOM). IOM might be the first OM available on early Earth for life and should provide information on solar system history. It is therefore essential to decipher the chemical structure of IOM.

IOM was isolated from the Murchison meteorite using successive water and solvent extractions and acid treatments (HCl, HF). Its chemical structure was investigated through a combination of various spectroscopic methods (Fourier transform infra-red, solid-state 13C and 15N NMR, electron paramagnetic resonance, X-ray absorption near-edge spectroscopy), chemical (RuO4 oxidation) and thermal (pyrolysis) degradations and high resolution transmission electron microscopy. The use of these complementary analytical tools yielded key information on the IOM structure at a molecular level and led to 11 quantitative parameters. A statistical model was therefore proposed for this molecular structure, fitting with these 11 parameters.

Moreover, deuterium isotope abundance was determined in individual compounds released through RuO4 oxidation and pyrolysis pointing to 3 types of H (aromatic, benzylic and aliphatic) with different D enrichment related to the C-H bond strength. This was further confirmed by laboratory experiments. We therefore propose that the IOM formed in a D-poor environment and was then transported and further enriched through exchange in a D-rich medium. EPR studies also revealed that free radicals were the hosts of extreme D enrichments revealed through nanoSIMS.

These results are difficult to reconcile with the usual interpretation according to which high D/H ratios represent survivals of interstellar grains. More likely, the deuterium-enrichment process took place after the formation of organic grains characterized by low D/H ratios, through an isotopic exchange-reaction with D-rich gaseous molecules, such as HD+ or HD2+. This exchange reaction most likely took place in the diffuse outer regions of the protoplanetary disk around the young Sun.

Element transport and mineral replacement reactions during alkali contact metamorphism

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To study element transport in crustal rocks, high concentration gradients are favorable, as they are present along the margins of peralkaline rocks intruded into common crustal rocks. The 1.16 Ga peralkaline Ilímaussaq intrusion in SW-Greenland is characterized by its high alkali as well as high LILE, HFSE and volatile content. It intruded at the contact between the granitic Julianehåb batholith and a volcano-sedimentary succession [1].

We took 19 samples along a 1 km long profile from the contact of the Ilímaussaq intrusion into the adjacent granite. Accounting for the exponential character of diffusive processes, we chose a close spacing between samples near the contact with increasing distances further away from the intrusion.

Significant contact alteration, accompanied by growth of new minerals (aegirine, arfvedsonite) has been previously reported [2] and can be observed in the field up to a distance of 40 m away from the contact. This is confirmed by stable isotopic data of Li and B [3, 4], supporting diffusive alteration of the contact rocks.

Our whole rock analyses reveal an influence of the alkaline fluids released by the Ilímaussaq complex on the host granite up to ca. 200 m by elevated contents of e.g. Na, Ca and P as well as depletion in Si and K. In addition, batches of eutectic quartz-feldspar intergrowths in the granite up to ca. 10 m from the contact imply partial melting of the granite.

Among the mineral replacement reactions the growth of amphibole and pyroxene at the expense of biotite as well as the replacement of perthitic alkalifeldspar by almost pure albite are most obvious. To get a full insight on replacement reactions and changes in mineral chemistry along the profile, microprobe analyses will be carried out.

Reconciling multiple constraints on late Cenozoic erosion and weathering fluxes: Can we do it?

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Records of geochemical tracers in late Cenozoic marine sediments show large changes, the causes of which have been the subject of intense interest in the geoscience community. Intensive tracers include $^{87}$Sr/$^{86}$Sr, $^{13}$C/$^{12}$C, $^{44}$Ca/$^{42}$Ca, $^{26}$Mg/$^{24}$Mg, $^{10}$Be/$^{9}$Be, $^{18}$O/$^{16}$O, $^{30}$Si/$^{28}$Si and $^{13}$C/$^{12}$O. Information from these tracers needs to be integrated with elemental mass balance constraints such as Mg/Ca in forams, sediment accumulation rates, changes in the CCD, and reconstructions of $p$CO$_2$. To date, a quantitative and self-consistent scenario that successfully integrates this diverse and increasingly detailed set of observations has been elusive. All of the isotopic tracers are subject to provenance effects, i.e., values can vary as a function of source, and the mix of sources changes in time. The stable isotope tracers are additionally subject to fractionation at the source via changes in weathering processes and/or biological cycling. They can be further impacted by fractionation during incorporation into sediment archives.

Studies at the small watershed scale suggest that several of the tracers ($^{87}$Sr/$^{86}$Sr, $^{26}$Mg/$^{24}$Mg, Ge/Si, $^{30}$Si) can be used to identify particular mineral weathering reactions and/or identify the effects of biocycling. Integrating this information over larger spatial and temporal scales is not straightforward. Biocycling effects can be important over short time scales but their impact is reduced over time scales much longer than the residence time of the tracer in regolith-soil-plant system.

Recycling of the sedimentary mass is a major source of the erosional flux, and can be particularly significant for tracers significantly stored in carbonate rocks, as these are nearly quantitatively recycled during erosion. While the late Cenozoic shift in $^{13}$C has received relatively little attention compared to some other tracers, a decrease in $^{13}$C$_{SW}$ beginning in the mid–Miocene is consistent with both a proportional and absolute increase in the weathering flux of carbonates. A mid-Miocene acceleration in sediment recycling appears at least consistent with most of the available constraints from other tracers of weathering and erosion, and a model can be used to make testable predictions for other tracer systems. Since each system is individually underconstrained, a quantitative approach that attempts to satisfy multiple tracer records is necessary.

Spatial vegetation patterns, catastrophic shifts and desertification in arid ecosystems under land use and climate regimes

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Desertification currently affects the livelihood of more than 200 million people. A primary aim of the international community is to stop desertification to enhance agricultural productivity and combat hunger of many millions of people. Desertification, especially the shift of productive semi-deserts into non-productive full-deserts, can have a ‘sudden’ or ‘catastrophic’ character, indicating the existence of critical transitions over ‘thresholds’ or ‘tipping points’.

These catastrophic events result from the interplay between two different ecological interactions among the plants making up the vegetation in semi-desert ecosystems. The first is facilitation, where plants support each other in terms of collectively attracting water and nutrients and provide the soil with organic matter compounds. Facilitation acts at relatively small spatial scales. Second, there is competition between plants for the same resources (water, nutrients), but then on a relatively large spatial scale. The process of facilitation helps plants to survive, together, under harsh conditions. Such survival under harsh conditions requires though a critical threshold. The model results closely resembled the patterns that were observed in the field trials.

We will present the outcome of a study in which spatial explicit models that simulate desertification is combined with field observations on semi-deserts under various land use and climate regimes. The results showed that particular non-random patterns in the spatial distribution of the vegetation are indicative the proximity of a critical threshold. The model results closely resembled the patterns that were observed in the field trials.

Bacterial cells can biosorb and accelerate the transport of heavy metals mixtures in soils

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Recent field observations have demonstrated that supposedly poorly mobile metals can be detected at long distances from their source, highlighting the importance of poorly predicted transport processes. The fast mobilisation of metals by the colloidal and mobile fraction of soils and in particular biotic colloids (bacteria, algae, fungi, virus, etc.), is now identified as an important secondary transport process that can lead, under specific conditions, to accelerated and potentially dominant pollutant transfer towards aquifers. In order to better understand the role of the bacterial compartment of soils to metal leaching, we conducted a coupled study under static and dynamic conditions. Firstly we evaluated Zn and Cd metal biosorption onto active or inactive Gram negative bacteria (Escherichia coli and Cupriavidus metallidurans CH34) by characterizing the sub-cellular distribution of the metals through a cell disruption approach. The quantification of Zn and Cd in extracellular, membrane and cytoplasm compartments of the cells permitted to show that metals are unequally distributed between the three cell compartments and also between the two bacteria. Surprisingly, metals internalization appeared to be the dominant accumulation process of metals (high cytoplasm contents). The physiological state of the cells was also shown to be important in metal management by the bacteria, since metal accumulation in active cells was reduced due to enhanced efflux and/or EPS production mechanisms. These results suggest bacteria can internalize important amounts of heavy metals and also that adsorption onto cell surface is only a first step in metal management by bacteria. The so-determined thermo-dynamic reactivity constants were used to fit metal breakthrough curves performed in natural sand columns. The transport experiments of bacterial cells, metals or mixtures of bacteria and/or metals performed in the second part of the study, demonstrated that bacteria are able to accelerate the in situ mobilization of Cd and Zn retained in natural sand columns. This transport process was shown to be dominant upon aqueous transport and was correctly fitted using a combined transfer and geochemical modeling approach. Altogether, these results showed that, under specific conditions, heavy metal transport by bacterial cells can dominate aqueous transport processes in soils.

Silicon stable isotope constraints on the global oceanic Si cycle

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The global oceanic distribution of nutrients such as silicon (Si) governs the distribution and magnitude of primary productivity in the sea, and thus the strength of the ocean’s biological carbon pump. These nutrient distributions are the combined result of biological and physical processes that interact over a range of temporal and spatial scales. Information on the stable isotope composition of dissolved nutrients can be employed to deconvolve the processes contributing to the observed oceanic tracer field, potentially allowing the identification of nutrient sources and/or the relevant biological–physical cycling processes.

We will present a dataset of the stable Si isotope composition of dissolved silicon (expressed as δ30Si) from three major oceanic regions: the Atlantic, the Southern Ocean and the South Pacific, including samples collected as part of the GEOTRACES programme. This high-precision dataset has been produced by a single laboratory, allowing a more robust assessment of intra- and inter-basin gradients than has been previously possible.

The coherence of the δ30Si distribution in the deep Atlantic is a testament to the strength of δ30Si as a tracer of the modern oceanic Si cycle. Values of δ30Si vary systematically with Si concentration, from +1.7‰ and higher in the Si-poor deep subpolar North Atlantic to values of +1.2‰ in the deep South Atlantic, associated with the mixing of water masses of Nordic and North Atlantic origin with Si-rich bottom waters from the Southern Ocean. The North Atlantic most likely owes its high-δ30Si signature to the input of 30Si-enriched silicic acid through the upper return path of the meridional overturning circulation (MOC), indicating that the basin-scale δ30Si gradient in the deep Atlantic is dominantly controlled by the interaction of biological Si utilisation with subsurface watermass formation in the Southern Ocean, and subsequent Si transport by the MOC.

In our presentation, we will extend our analysis of oceanic δ30Si in the MOC context to the global ocean, including the interpretation of our dataset in the framework of geochemical box models of the ocean.

Mineralogical Magazine www.minersoc.org
Use of stable (HOCN) and radiogenic (Sr) isotopes to determine the geographic provenance and traceability of artisanal cheeses of Quebec, Canada

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Introduction

Analysis of stable isotopes has often been used to determine the traceability of different food products [1] The light stable isotope ratios in dairy products such as cheese can provide information for tracing geographical origin,[4] The province of Quebec is Canada’s largest cheese producer and artisanal cheeses are becoming a larger part of this market. In this context, we selected artisanal cheeses from six different regions of the province of Quebec to study the applicability of light stables isotopes and radiogenic isotope (Sr) ratios as discriminants to provide geographic traceability.

Sampling method and results

The cheese samples were analysed for light stable isotope ratios (HOCN) which are mainly influenced by altitude, distance from the sea, use of fertilizer, rainfall, food type, temperature, longitude and latitude [2,3,6]. The Sr isotope analyses are indicative of the geology of the type of substrate of the grazing areas [5]. Preliminary results yield \(^{87}\)Sr/\(^{86}\)Sr ratios that vary from 0.71084 to 0.71347. These values reflect soils composed largely of galcial tills derived from either the Canadian shield or Appalachain Orogen. Stable isotope \(^{18}\)O values vary between -103.06‰ to -55.74‰, and \(^{13}\)C between -17.99‰ to -7.54‰. In addition, samples of the food, water, soil and raw milk will also be analysed to determine if enrichment or depletion of the different stable isotope ratios occurs during the manufacture of milk and during the conversion of milk to cheese.

Indian Ocean monsoon dynamics recorded in a speleothem from Socotra, Yemen

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On the arid Indian Ocean Socotra Island (12º30’36” 53º55’12”), the Intertropical Convergence Zone (ITCZ) induces a bimodal distribution of the precipitations. Rain falls only as the northward migrating ITCZ passes in May-June and as it returns southward from September to December. The watershed effect of the 1540m-high SW/NE oriented Haggeher Mountains forces precipitations to concentrate on the windward side of the range [1]. Multi-proxy analyses (\(^{18}\)O, \(^{13}\)C & greyscale) are carried out at high resolution (500µm = time-scale ~3 years) on two stalagmites collected in the eastern part of the island: STM1 from the Hoq Cave and STM5 from Casecas cave, 6 km away. Based on TIMS U/Th-dating they resp. cover the last 6000 years and the last 1000 years. Spectral analysis of the obtained records reveals an important ~205-years component in STM1. Comparing the \(^{18}\)O & \(^{13}\)C records with a reconstruction of solar activity [2] indicates that for most of the last 6000 years periods of lower precipitation and less vegetation are associated with periods of high solar activity. Periods of low solar activity induce more precipitations and higher vegetation abundance. In Oman, solar activity is positively related with the intensity of the rainy seasons because of changes in the latitudinal position of the ITCZ and the convective activity [3]. The Socotra results independently confirm this hypothesis and refine it by identifying the 205-years “De Vries / Suess” sunspot cycle as the dominant forcing cycle for the Indian Monsoon Dynamics on a centennial scale.

**Evolution of crust in the Dharwar craton: The Nd isotopic evidence**

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The western and eastern Dharwar cratons (WDC and EDC) show appreciably different crustal evolution patterns as recorded by 333 whole-rock Nd isotopic data (including 34 unpublished data of the author). Both the cratons exhibit evidence of Palaeoarchaean crust (Fig. 1) whose rock record is either destroyed by later crustal reworking or awaiting to be discovered. In EDC 3-2.7 Ga is the most significant crust extraction period, whereas in WDC crust was extracted in two dominant episodes i.e. 3.5-3.2 and 3-2.9 Ga. Some komatiites and mafic volcanics of the older episode have considerably higher $^4$Nd values (>4.5) indicating that at least parts of the contemporary mantle was extremely depleted possibly due to extraction of crust during some earlier event(s). Younger mantle-derived rocks in the WDC (especially the 2.9 Ga mafic volcanics) do not show evidence of such extremely depleted mantle. This requires immediate refertilization of the mantle below WDC after the older episode of crust formation (~3.2 Ga). The Neoarchaean period in the WDC is characterized by some juvenile addition of crust and extensive crustal recycling during 2.7-2.6 Ga. For EDC contrasting source characteristics of contemporary mantle-derived Neoarchaean rocks (extremely depleted to chondritic mantle) suggests juxtaposition of unrelated terranes by accretionary processes. The terminal Neoarchaean in EDC is characterized by granitoid formation from metasomatized mantle wedge as well as widespread crustal recycling.

![Figure 1: Distribution of depleted mantle model ages in the eastern and western Dharwar cratons.](image)

**Isothermal, kinetic and mechanism studies of uranium biosorption by Aspergillus niger from aqueous solutions**

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Biosorption have emerged as an alternative technology for heavy metal and radionuclide removal from ground water contaminated due to mining sources [1, 2]. In light of this, present study has been carried out to investigate the biosorption potential of *Aspergillus niger* for removal of uranium form aqueous solution. Some concerned results are shown in Fig. 1.

![Figure 1: Effect of Biosorbent dose on biosorption of U (VI) on non-living A. niger biomass.](image)

**Discussion of Results**

Uranium uptake at pH 5 and 100 µm particle size, Adsorbent dose of 10g/L and initial metal concentration of 100mg/L. Maximum uptake of 9.21 mg/g was observed after the Contact time of 75 minutes. Equilibrium data fitted well to Langmuir model and Uptake kinetic followed pseudo-second order model. Base treatment was found to enhance the metal removal ability of untreated biomass. The mechanism of process was gained by FTIR and SEM. IR spectra analysis revealed that Carbonyl and amino groups have played important role in U (VI) biosorption. The results are well in concordance with some earlier findings in that concern [3, 4].

Growth and reworking of Gondwana through time

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The timing of continental crust generation is dependent on the nature of the rock record. Juvenile igneous rocks from various continental segments usually show marked age peaks suggesting episodic growth [e.g. 1]; and fine-grained sediments, which provide an average of their igneous source terranes, provide smooth curves of crust generation [e.g. 2], which are more consistent with the continuous nature of crust formation at the level of destructive plate margins. Thus there are long-standing questions over (i) whether the age peaks of juvenile rocks are representative, or merely artefacts of selective preservation [3], and (ii) the extent to which the processes and rates of crust generation and recycling have varied with time.

We present an integrated U-Pb, Hf and O isotopes study on zircons from sedimentary deposits along ~2000 km of the eastern Australian coastline. The data establish that continental growth of Gondwana is continuous, with a significant inflection point in the rate of generation at around 3 Ga. This point marks the transition between (i) very rapid generation of continental crust in the first ~1.5 Ga of Earth history and (ii) lower volumes of preserved crust towards the present day. Such a fundamental change in the way the continental crust was generated and preserved can be linked to the onset of ‘modern’ plate tectonics, which may have been active since at least 3.1 Ga [4]. This is also consistent with the formation of Hadean/Early Archean crust in a tectonic environment different from modern plate tectonics [5].


Soil closure ages from meteoric 10Be, McMurdo Dry Valleys, Antarctica

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Understanding Neogene polar climate in the McMurdo Dry Valleys relies largely on evidence from landscape evolution, glacial modelling and stratigraphy. We provide new evidence from meteoric 10Be for the onset of frozen, hyper-arid conditions in Dry Valley soils. A simple decay model for the co-occurrence of 10Be and illuviated clay in two adjacent profiles indicates the clays were actively migrating down from the surface in a warmer climate until the system froze between 6 and 9 Ma. The model also suggests denudation rates of 0.02-0.06 m Myr⁻¹ since closure. These data provide an independent test to glacial-stratigraphic evidence used to determine Antarctic paleoclimate.

Clays bound with meteoric 10Be are prevalent in many Dry Valley soils to depths of over 4 m. These particles, which are now frozen in place, were illuviated by percolating water from the surface, during a previous ‘wet period’. We use two adjacent profiles to take advantage of the 10Be clock and determine when 10Be was sealed or closed off from the surface. The two-profile method allows elimination of several variables and hence, calculation of how long 10Be has been in the soil since freezing or closure. By sampling soils at a variety of altitudes and locations, we may build up a better picture of the transformation from sub-polar to polar conditions in the Dry Valleys.
Ocean oxygenation during the PETM: Mo isotope data from the Arctic and Tethyan Oceans

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Evidence for ocean deoxygenation during past intervals of global warming can help to set observations of expanding oxygen minimum zones in the modern oceans into a longer term geological context. The molybdenum (Mo) isotope composition of the hydrogenous Mo in marine sediments that accumulated in euxinic settings can preserve the seawater Mo-isotope composition, which in turn reflects the balance between oxic, anoxic, and euxinic sinks in the global ocean. As such, it can be used to determine the extent of deoxygenated waters in past oceans when the local depositional environment is well characterised.

We present new Mo isotope data of samples from Arctic Ocean IODP Site 302 and from continental shelf sites on the northern Tethyan margin (Guru Fatima and Kheu River) that accumulated during the Paleocene-Eocene Thermal Maximum (~56 Ma ago). The PETM is characterised by a global C-isotope excursion (CIE) caused by the introduction of a large amount of isotopically depleted carbon into the earth-ocean-atmosphere system, which in turn caused global temperatures to rise by 5-8°C.

Mo isotope data from IODP Site 302 broadly mirror the organic carbon isotope excursion recorded in the same sample suite, with near uniform values of 2.1‰ during the peak of the CIE and lower values during the late Paleocene and during the PETM recovery interval. Samples that accumulated during the peak of the CIE were deposited under locally euxinic conditions, demonstrated by trace element data measured in the same samples and also by comparison to published organic geochemical data. Their Mo-isotope values consequently record the seawater value at this time, which was only ~0.2‰ lower than modern seawater (~2.3‰). This finding suggests that (1) once euxinia in the Arctic Ocean is accounted for, global ocean anoxia was not widespread during the PETM and (2) the Arctic ocean was unrestricted during the PETM.

In contrast, preliminary Mo isotope data from the northern Tethys Ocean suggest a slight expansion of ocean anoxia at the onset of the CIE, an interval that is missing within the Arctic core.

Hydrogen sorption by synthetic montmorillonites and clayrock at high temperature

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Hydrogen is more and more studied as a future energy carrier due to its availability and its energy capacity. The montmorillonite clay minerals are recognized as good hydrogen adsorbents [1] due to their large specific surface area and their wide range of porosity. In addition to this application, a clayrock has been considered as a host rock for French nuclear waste and particularly the Callovo-Oxfordian (COx), principally constituted by smectite and illite clays.

Regarding nuclear waste repository, hydrogen gas is expected to develop from the anaerobic corrosion processes of the waste containers after the disposal closure. It is therefore of fundamental importance to study the fate of the hydrogen gas produced in the system, in terms of reactivity and integrity of the surrounding claystone layer.

This study aims at investigating hydrogen sorption on different types of synthetic montmorillonites and COx clayrock using gas chromatography and Sievert technology. Two-month long experiments were carried out at 90°C (the maximum temperature in the waste repository site) with dried or saturated clays. The hydrogen partial pressure varies from 0.1 to 0.45 bars.

Dried experiments show a sorption of hydrogen amount of 0.13 wt%. Experiments with saturated clays highlight a decrease of headspace hydrogen pressure (the figure below) as a function of time for a COx powder in NaCl aqueous solution taking into account the dissolved hydrogen. Sievert technology using high pressure of pure hydrogen gas (up to 80 bars) at 90°C shows a maximum sorption of 0.20 wt% for synthetic montmorillonite and 0.16 wt% for COx sample.

![Figure 1](https://pubs.geoscienceworld.org/minmag/article-pdf/75/3/712/2918898/gsmminmag.75.3.04-D.pdf)

**Figure 1**: Evolution of hydrogen relative pressure with time for clay fraction of a COx sample at T = 90°C

The effect of size on nanoparticle dissolution rate
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The dissolution rate of nanoparticles affects both their persistence in the environment and the release rate of their metal content, and, hence, can control their toxicity. While previous studies concluded that nanoparticles dissolve faster than their bulk analogs, contradictory evidence suggests that nanoparticles dissolve more slowly. Furthermore, insufficient characterization of the nanoparticulate samples and the solution chemistry in past studies obscures the relationship between particle size, surface area, and dissolution rate. There is a critical need for additional studies, using well-characterized nanoparticles and reactive solutions, to develop a model of nanoparticle dissolution rate.

Dissolution rates are a function of both the distance from equilibrium (providing the driving force for dissolution) and a dissolution rate constant (reflecting the dissolution mechanism and the strength of bonds critical to maintain the structure). The current study takes the approach of studying dissolution rates at far-from-equilibrium conditions to quantify the effect of particle size on the dissolution rate constant, isolating any potential kinetic effect of particle size from the well-established effect of particle size on solubility.

Multiple samples of both nanotalc and amorphous silica nanospheres were synthesized, ranging in size from approximately 20 to 200 nm. Samples were characterized by XRD, SEM, TEM, dynamic light scattering, and gas adsorption. Flow-through experiments were performed at far-from-equilibrium conditions with pH from 2-10. Batch experiments were performed at both far-from and approaching equilibrium.

Preliminary interpretation of these data suggests that any effect of size on dissolution kinetics is minor. Thus, as the dissolution rate constant appears to be size independent (within experimental error), the dissolution rate of nanoparticles as a function of size and departure from equilibrium can be modeled by using classical kinetic rate laws and taking account of the effect of size on solubility.

Marine redox conditions and sulfur cycling during the deposition of the 2.3 Ga Timeball Hill Formation
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Rhenium and Molybdenum concentrations in shales and sulfur isotopes in disulfides and organic matter provide new insights in the development of the ocean-atmosphere system during the deposition of the 2.3 Ga Timeball Hill Formation, South Africa. Relatively low enrichment factors (relative to average crustal abundances) of Mo between 0.1 and 2.4 and high Re enrichment factors between 1.1 and 25.0 can be distinguished. Marginal concentrations of Mo correlate with the highest enrichments of Re, and appear to be coupled to the most negative δ34S values (down to -30 ‰ against V-CDT in disulfides) and highest concentrations of organic bound sulfur.

High Re concentrations over wide parts of the stratigraphy argue for a deposition under anoxic but, as indicated by low Mo concentrations, not for euxinic deepwater conditions. Pyrite from these stratigraphic levels show the lowest δ34S values, thus high isotopic fractionation, which suggests the establishment of an oceanic sulfate pool. The absence of large Mo and Re enrichments in the middle parts of Lower and Upper Timeball Hill shales indicate potentially oxic oceanic conditions. These samples show high δ34S values in disulfides which could indicate a low sulfate flux to the oceans.

These observations lead to the conclusion that the water column was constantly non-euxinic at 2.3 Ga. The intensity of continental weathering and the subsequent delivery of nutrients to the oceans was variable and a consequence of the fluctuations of the atmospheric oxygen content.
Structural incorporation of selenium in iron sulfides

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One of the key issues regarding the disposal of high-level nuclear waste in deep geological formations is related to the long term safety of a waste repository. Different performance assessment calculations for such repositories show a domination of 35Se radionuclide with regard to the total exposure to the biosphere in the period of 10^4-10^6 years after disposal. Selenium is often associated with sulfides such as pyrite, a frequent minor constituent of host rocks and bentonite backfills considered for radioactive waste disposal. In this study, we investigated the incorporation of Se(-II) and Se(IV) into pyrite.

The syntheses occurred via direct precipitation in batch and as coatings on natural pyrite in mixed flow reactor (MFR) experiments under anoxic conditions for Se-concentrations in the solutions up to 10^{-3} molL^{-1}. Furthermore, a high temperature synthesis by chemical vapor transport enabled the synthesis of Se-dotted pyrite for single-crystals with a size up to 1 cm.

The mineralogical analyses by SEM and XRD reveal the syntheses of pure phases. Neither achavalite (FeSe), nor ferroslite (FeSe_x) were detected. The average of Se-uptake in 34 samples in batch experiments has been 98% and in MFR syntheses 99.5%, indicating a high potential for the retention of selenium by pyrite.

XAFS investigations have been performed at synchrotron light facility ANKA, Karlsruhe. These analyses and additional XPS measurements point out a reduced valence state of Se by initially dissolved Se(-II) and Se(IV) coprecipitated in pyrite and mackinawite. Curve progression and k-edge values [1,2] for selenide dotted mackinawite (E_0: 12655.3 eV) in batch experiments imply a valence state of Se(-II) and for selenide dotted pyrite (E_0: 12656.9 eV ± 0.3) in batch experiments a valence state of Se(-I), while the k-edge value of Se(0) as reference is higher (E_0: 12658.0 eV).

XAFS analysis on the coatings from MFR-syntheses, performed under slightly supersaturated conditions, indicate a coprecipitation of Se(-II) and Se(IV) predominantly as Se(0). With regard to batch experiments, these results indicate a substitution of sulfur with selenide just for highly supersaturated solutions. In selenide dotted mackinawite via direct precipitation in batch experiments occurred a substitution of S with Se in an achavalite-type compound. As well, S is substituted by Se in selenide dotted pyrite, ending in a FeSSe compound which could be best described by a slightly distorted pyrite structure.


Geochemical expression of buried iron-oxide Copper Gold mineralisation within physical and chemical interfaces of the deep cover at the Hillside Prospect, South Australia

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Iron-Oxide Copper Gold (IOCG) mineralisation is an economically important mineral system in Australia, and includes the enormous Olympic Dam resource. Relative to its economic significance, however, little is known about the regolith geochemical expression of IOCG mineralisation, and therefore geochemistry has been under-utilised within the exploration for further deeply (10s-100s metres) buried deposits. This study shows that the weathered and transported cover overlying buried mineralisation can host systematic geochemical expressions of buried IOCG mineralisation.

The Hillside Prospect is 100 km northwest of Adelaide within the southern end of the IOCG prospective, eastern Gawler Craton. Mineralisation here is associated with N-S trending structures of the Pine Point Fault Zone.

Surface (soil) geochemistry results have shown locally elevated Cu-Au concentrations overlying buried mineralisation. The processes and associations with the underlying mineralisation and parts of the 10s-100s m deep cover in between the mineralisation and the soil are poorly constrained. Coastal cliffs in the area expose buried mineralisation at 10s of metres depth and the overlying saprolite, palaeodrainage, marine and aeolian sediments. Multi-element geochemical characterisation of these profiles shows variations in the chemical parameters associated with physical interfaces (e.g. unconformities and sediment lithologies) and chemical interfaces (e.g. palaeo- and contemporary redox boundaries, watertables) that provide strong expression and contrast within the cover for settings laterally proximal or distill to mineralisation. Many of the chemical interfaces are associated with supergene halos that are organised into locally enriched and differentiated U, Au and Cu zones flanking mineralisation. Whilst redox conditions and secondary iron oxide hosts provide important constraints on this geochemical expression, the secondary carbonate minerals and deep-rooted plant biogeochemical processes are also important.
Os isotopes in detrital Os alloys from the Rhine and evidence for a 1.2-1.3 Ga global? mantle melting event

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Osmium isotope ‘dating’ of large populations of mantle-derived osmium-bearing alloys provides a key test for the idea of episodic crustal growth linked to global mantle melting events in Earth history [1]. Os alloys are formed within the mantle during high-degree melting, and their 187Os/188Os isotopic ratio can be used to date their formation.

Over 200 detrital Os alloys from placer gold occurrences in the Rhine between Basel and Frankfurt were obtained by gold washing techniques and hand-picking from gold separates. These 20-300 µm detrital Os alloys are derived from outcrops of ultramafic rocks in the Alps, which include blocks of mantle rocks with Tethyan affinity such as the Totalp Massif, and ultramafic lenses of unknown blocks of mantle rocks with Tethyan affinity such as the Totalp Massif, and ultramafic lenses of unknown... (Precambrian?) age in the Gotthard and Aar Massifs. Another source may be the Molasse of the Alpine foreland basin. 187Os/188Os isotope ratios were measured by LA-MC-ICPMS, to determine Re-depletion ages that should constrain the ages of melting in the mantle source rocks. The data show distinct age peaks at 0.5 and 1.2-1.3 Ga.

The 1.2-1.3 Mesoproterozoic age peak recorded by the Rhine Os alloy population does also occur in Os alloy age distributions of other ophiolites worldwide, generally as a subsidiary peak [1]. We show that the Mesoproterozoic age is also prevalent in Re-depletion age distributions of whole rock samples of refractory mantle xenoliths from ocean islands, and whole-rock samples of anomalously depleted abyssal peridotites from modern oceans, e.g., from the 15-20 Fracture Zone (MAR) and Macquarie Island [2]. Therefore, analysis of Re-depletion ages from mantle rocks worldwide collectively point to a Mesoproterozoic, 1.2-1.3 Ga high-degree mantle melting event of global significance. This event may be related to a slab-avalanche or whole-mantle overturn event in Mesoproterozoic times.


Adsorption of a textile dye (Acid Red 88) by montmorillonitic clay: Estimation of equilibrium, kinetic and thermodynamic parameters

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Introduction
Textile dyes are one group of the pollutants and the presence of dyes in the aquatic environment has been of great concern because of their potential health hazards associated with the carcinogenic, mutagenic, allergic and toxic natures as well as negatively effects on the photosynthetic activity in aquatic life [1].

Method
The adsorption of AR88 onto montmorillonite was studied with variation in the parameters of pH, contact time, adsorbent and dye concentrations, and temperature to estimate the equilibrium, kinetic parameters and thermodynamic [2].

Kinetic models including pseudo-second-order, pseudo-nth-order, Bangham and double-exponential models were selected to follow the adsorption process. Kinetic parameters such as the rate constants, the equilibrium adsorption capacities and the related correlation coefficients, for each kinetic model were calculated and discussed. Thermodynamic parameters such as activation energy (Ea), Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also evaluated.

Discussion of Results
The dynamic data were fitted well the pseudo-nth-order kinetic model and also followed double-exponential function, the pseudo-second-order and Bangham Model, respectively.

The adsorption data obtained were well described by the Langmuir isotherm model. The maximum adsorption capacity was found to be 588 mgg⁻¹ from the Langmuir isotherm model at 20 °C. The negative value of change in Gibbs free energy indicates that the adsorption is spontaneous. The results show that montmorillonitic clay could be employed as low-cost material for the removal of acid dyes from textile effluents.

Geochemical and tectonic fingerprinting of ophiolites

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We present a new classification of ophiolites, incorporating the diversity in their structural architecture and geochemical signatures that result from the variations in petrological, geochemical and tectonic processes during formation in different geodynamic settings. We define ophiolites as suites of temporally & spatially associated ultramafic to felsic rocks related to separate melting episodes & processes of magmatic differentiation in particular tectonic environments. Their geochemical characteristics, internal structure and thickness vary with spreading rate, proximity to plumes or trenches, mantle temperature, mantle fertility, and the availability of fluids. Subduction-related ophiolites include suprasubduction zone and volcanic arc types, whose evolution is governed by slab dehydration and accompanying metasomatism of the mantle, melting of the subducting sediments and repeated episodes of partial melting of metasomatized peridotites. Subduction-unrelated ophiolites include continental-margin, mid-ocean ridge (plume-proximal, plume-distal and trench-distal), and plume-type (plume-proximal ridge and oceanic plateau) ophiolites that generally have MORB compositions. Subduction-related ophiolites develop during the closure of ocean basins, whereas subduction-unrelated types evolve during rift-drift and seafloor spreading. Geochemical and tectonic fingerprinting of Phanerozoic ophiolites within the framework of this new ophiolite classification is an effective tool for identification of the geodynamic settings of oceanic crust formation in Earth history that in turn helps us deduce the processes by which these oceanic rocks were incorporated into continental margins. We apply this new ophiolite classification to Precambrian greenstone belts as a conceptual framework to examine potential vestiges of Proterozoic and Archean oceanic lithosphere.

Protection of organic matter by clay minerals in source rocks revealed by biomarker analysis

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Several mechanisms have been proposed in description the accumulation and preservation of organic matter(OM) in sediments, and the adsorption of clay minerals is concerned as an important way. It is significant that these different occurrences of OM studies with the biomarker information obtained from an source rock. The 10 source rock samples, an depth interval from 1294 to 3357 m from Shayejie formation in Dongying depression of China, were collected. The clay size fraction (<2 µm) were isolated by sedimentary approach after the dispersion of the source rock by ultrasonic and deionized water. Both the clay size fraction and bulk source rocks were extracted by dichloromethane, and GC/MS was applied.

The normalized amount of the extractable organic matter (EOM) is higher in clay size fraction than it in the whole rock, 0.56mg/g and 0.37mg/g respectively, although the composition are similar between them. This suggestes that EOM mainly occurred as combined with clay size fraction in source rocks. The biomarker data show that there is no notable difference on characteristics of OM associated with clay fraction and in the whole rock. However, the differences between clay size fraction and whole rock show that the weak degradation of OM combined with clay fraction occur no matter caused by micro-organisms or thermalism, which could be demonstrated by the relative abundance of alkanes and isoprenoids (Pr/nC17 and Ph/nC18 ratios are 1.44 and 1.54 in mean for the whole rock while 1.33 and 1.2 in mean for clay size fraction) and the ratios of maturity parameters(such as C18/22S/S+R ratios are 0.46 and 0.41 in average respectively, C29/C20 20S/20(S+R) ratios are 0.18 and 0.14 in average respectively, for the whole rock and clay size fraction). In addition, the information acquired from biomarker of the whole rock may be obscured for the variety occurrences of OM in the whole rock, which should be caution.

This research was supported by the National Natural Science Foundation of China(Grants 40872089 and 41072089) and the State Key Lab. of Marine Geology Fund, Tongji University (MG200902).
Application of the field seismic data in superficial structure study for Wenshui Area

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The Wenshui area is located in the middle-west of Shanxi Province in north China, where plenty of coal resources are mined. In recent years, a large amount of seismic exploration work with the aim at coal resources has been done in the area successively. Based on the foundation of seismic exploration data, this study focuses on the superficial structure of sedimentary basin in the Wenshui area.

A 3D seismic data acquisition had been done in the Wenshui area. Seismic exploration lines are little longer than the field survey profile to cover all the possible coal resources area. In order to obtain the superficial structure of the area, seismic data processing had been done. And it can be summarized concisely into the following steps [1]: (1) carefully checked the positions of field shot-receiver pairs to obtain accurate localities; (2) calculated the static corrections in details; (3) eliminated bad shots, bad courses and abnormal amplitudes; (4) selected appropriate deconvolution parameters; (5) made accurate velocity analysis and got residual static corrections through stacking; (6) carried out the post stack processing and precise migration.

The result shows that there is a large syncline structure in the centre of the region, suggesting long-term tectonic push influenced Wenshui area since Triassic. This crustal deformation was accompanied with rock cracking in both coal sills and their wall rocks, which could lead to potential danger to the deep exploitation for coal mines.

This study is supported by Teacher Foundation of China Earthquake Administration (No: 20090112)


Silicon isotope composition of chert in carbonate rocks, as an indicator of paleo-environmental variation in ocean

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An investigation on the silicon isotope variation of chert bands and nodules in carbonate sedimentary formation from early Proterozoic to Mesozoic is undertaken in this study to study the temporal variation of the environmental conditions of the ocean.

The cherts in carbonate formation of Proterozoic period show large variation on their silicon isotope compositions. The δ30Si values of chert from early Proterozoic Futuo Group vary from 0.1‰ to 1.3‰, with an average of 0.76‰, whilst those from middle Proterozoic Changcheng Group vary from 1.1‰ to 3.4‰, with an average of 2.09‰. The chert from late Proterozoic strata has lowest δ30Si values, varying from 0.0‰ to 0.9‰ and with an average of 0.36‰.

The cherts in carbonate formation of Palaeozoic and Mesozoic periods show smaller δ30Si variation than for Proterozoic. The chert of early Palaeozoic shows δ30Si values from -0.6‰ to 1.7‰, averaging 0.70‰. Similarly, the chert of late Palaeozoic shows δ30Si values from -0.4‰ to 1.7‰, averaging 0.61‰. Furthermore, the chert of Mesozoic shows δ30Si between -0.3‰ and 1.1‰, averaging 0.55‰.

The positive δ30Si values observed in all cherts in the carbonate formation from Proterozoic to Mesozoic indicate that the ocean has positive δ30Si value since early Proterozoic period. This may be caused by the increase of biological activities, which generate silicon isotope fractionation while reduce the silicon content in the ocean water. The higher and more variable silicon isotope compositions of Proterozoic chert may reflect the significant change of environment conditions (temperature and Si content) in ocean from Archean to Proterozoic.
Volatile and viscosity

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The physical properties of magmatic melts are notably influenced by the presence of dissolved volatiles. The influence of volatiles on the PVT-equation-of-state of silicate melts is slowly being mapped out in terms of the molar volume and its temperature- and pressure derivatives. The influence on transport properties is, to date, better constrained, and indeed the effects are even more dramatic for some volatiles. In both cases a wide range of complementary experimental techniques are being applied and it is often the case that proxy methods for property determinations yield results where direct determination is experimentally hindered.

Perhaps the most exhaustively investigated example of the influence of volatiles on properties is the case of the influence of water on viscosity. Its extensive investigation in the past 20 years contains many examples of experimental foresight and advance, as well as a number of pitfalls. Using this example, together with the allied determinations of transport properties in melts, a sketch of the state-of-the-art will be attempted.

An example of fluid immiscibility during the subvolcanic emplacement of a boron-rich acidic melt: The Capo Bianco aplite

Elba Island, Italy

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Very unusual melts rich in boron and other volatile and rare elements are produced during partial melting of continental crust as well as by differentiation of granitoid plutons. Commonly these melts crystallize at plutonic depths producing typical coarse-grained rocks (pegmatites) that are industrial sources for rare elements (e.g. Ta, Li). Sometimes, such melts produce intrusive bodies showing a fine grained microgranite-aplite texture. In both cases the final equigranular isotropic texture reached by these rocks masks the original structure of magma (e.g. presence of early phenocrysts) and the eventual dynamic patterns experienced during transfer and emplacement of magma.

The Capo Bianco aplite sill (Elba Island, Italy) was emplaced at shallow depth (≈ 2.6 km) in the Late Miocene, recording very peculiar petrographic (layered and oriented texture) and geochemical features that recall a fluid immiscibility process between silica-rich and boron-rich melts. The rapid crystallization of the peraluminous, boron-rich Capo Bianco aplite allowed the preservation of the original structure of the acidic magma with a small percentage of early, millimetric phenocrysts (quartz, K-feldspar, oligoclase, muscovite) into a very fine-grained quartz-feldspatic groundmass. The groundmass also hosts a large number of spherical-ellipsoidal tourmaline orbicules ranging in size between few mm up to 15 cm. The tourmaline orbicules are made up by fibrous-radiating schorl-elaibite needles and quartz. Their textural relationships with the host, internal textural and chemical-isotopic features suggest that they represent an early character of the magma and excludes their formation by late- to post-magmatic processes. This observation coupled with geochemical composition of the rock and available experimental data on silicatic melts/glasses indicate that tourmaline orbicules can represent the product of rapid crystallization of boron-rich silicate melt bubbles earlier separated from the acidic magma before the final emplacement. Capo Bianco aplite can thus be regarded as a serendipitous occurrence of a boron-rich magma that escaped the source region and stopped/crystallized in a subvolcanic setting, just at the right depth for maintaining a snapshot of the silicate-liquids immiscibility processes and the emplacement dynamic.
Coupling isotope labeling with compound specific stable isotope analysis of microbial biomarkers

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The vast number of high molecular substances in soil and their specific degradation pathways all end up in a reasonable small number of low molecular substances (LMWOS). Thus, the transformation and fate of LMWOS is one of the most important processes in biogeochemical cycles. These transformations are mainly controlled by microbial utilization and thus coupling the fate of LMWOS with their use by microbes is one of the tasks in the elucidation of C and thus coupling the fate of LMWOS with their use by microbes is one of the tasks in the elucidation of C transformations and cycles.

Therefore we performed field experiments including application of dual-labeled and uniformly or position-specifically labeled amino acids. The microbial utilization was measured by means of 13C- and 15N-analysis of microbial biomass with the chloroform-fumigation-extraction method. A more specific look on the utilization of individual amino acids or C positions by distinct microbial groups was gained by the 13C-PLFA approach.

Comparison of 13C- and 15N-incorporation revealed, that for a well N-supplied microbial community (C:N~6) of a grassland ecosystem approx. 50% of the amino acid N is mineralized by the microbes, whereas the remaining amino acids were incorporated into the microbial biomass. Incorporation of amino acid C into microbial biomass was highest for osmotrophic, prokaryotic groups. Position-specific labeling showed that highly oxidized groups are preferentially degraded, whereas more reduced C positions showed higher incorporation into the microbial biomass.

Our results show, that the combination of labelling with compound specific isotope analysis of microbial biomarkers opens a new way to investigate the microbial transformations of LMWOS in soil. Especially investigating the utilization of individual C atoms by microbial groups allows conclusions about the mechanisms and kinetics of microbial substrate utilization and the interactions between these groups. This will improve our understanding of soil carbon fluxes.

Control of biomineral formation during microbial Fe(III) reduction by local Fe2+ gradients – A multiscale approach

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The identity of minerals formed as a consequence of microbial iron(III) reduction is a function of geochemical conditions and microbial metabolic activity. While geochemical conditions set a thermodynamic framework for biomineralization, the microbial cells can influence the mineralization product by providing templates for mineral nucleation, localization of mineral precipitation, production of electron shuttles and changing the rate of Fe(III) reduction. Local Fe(II):Fe(III) ratios are known to be a key parameter for the transformation of Fe(III) minerals such as ferrihydrite to either dissolved Fe2+, Fe(II) minerals (siderite), Fe(II)/Fe(III) minerals (green rust or magnetite) or other Fe(III) minerals (goethite).

We showed that under identical total concentrations of Fe(II) minerals, the geometry of the experimental setup significantly affected the local geochemistry, iron reduction rates and mineralogy of the reduction products in experiments with the iron-reducing strain Shewanella oneidensis MR-1. In these setups, the bacteria reduced 2.5 to 15 mM ferrihydrite with lactate as electron donor in glass tubes that were stored either horizontally or vertically.

In all setups with >7.5 mM ferrihydrite, magnetite formation was observed probably due to a high Fe(II):Fe(II) ratio present during ferrihydrite reduction. At lower concentrations of ferrihydrite, no magnetite but rather dissolved Fe2+ and/or siderite were formed in horizontally incubated tubes. However, in vertically incubated tubes magnetite was formed even at ferrihydrite concentrations as low as 2.5 mM. Probably ferrihydrite accumulation at the bottom of vertically incubated culture tubes also led to high Fe(II):Fe(II) ratios allowing magnetite to form. A multiscale approach combining bulk analysis with high resolution geochemical measurements and confocal laser scanning microscopy allowed us to characterize the microenvironments, localize cells at the mineral-solution interface and correlate geochemical data to mineral identification by XRD and Mössbauer spectroscopy.
Molecular microstratigraphy via laser-desorption ionization Fourier-transform ion cyclotron resonance mass spectrometry (LDI-FT-ICR-MS)

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Ultrahigh-resolution mass spectrometry via the Fourier-transform ion cyclotron resonance technique (FT-ICR-MS) offers fundamentally new insights into the molecular world of natural waters. Oceans and freshwater systems are among the most complex molecular mixtures on Earth, containing tens of thousands if not millions of different compounds, collectively known as dissolved organic matter (DOM). With help of FT-ICR-MS, DOM can now be appreciated in its full molecular complexity, and a holistic geo-metabolomic approach is in sight that will allow a mechanistic understanding of element cycles in the ocean. In sediments and soils similar progress has been hampered by limited capabilities for the ionization of organic matter from solid samples for FT-ICR-MS analysis. In the life sciences, different laser-desorption ionization techniques (LDI) coupled to FT-ICR-MS are established tools for the molecular characterization of metabolites in organic tissues. Recently, this technique was extended for two-dimensional imaging of organic tissues allowing the identification of specific metabolites on a micrometer spatial scale. Objective of our study was to apply LDI-FT-ICR-MS for the molecular imaging of sediments. We obtained detailed molecular fingerprints of finely layered marine sediments, spatially resolved on a 50 micrometer scale. These first molecular images of marine sediments illustrate the enormous potential of LDI-FT-ICR-MS for the geosciences. Instead of targeting a small number of specific biomarkers, molecular formulae of hundreds to thousands of individual compounds are simultaneously obtained. Micrometer-scale stratification can be resolved on an extremely small amount of sample which is otherwise not accessible to molecular analysis.

Origin of iron layer in sediment of Lake Superior: Abiotic vs. biotic

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In spite of being the largest by surface and one of the most oligotrophic fresh water bodies in the world, Lake Superior is rather a blank spot on the map of modern Geochemistry and Geomicrobiology. Although the limnological puzzels of Lake Superior are increasingly attracting scientists [1], very little is known about the sediments and their associated microflora. In this study we investigated geochemical and microbiological processes that may lead to the formation of a two cm thick iron layer about 10 cm below the sediment surface. Sediment cores from two stations (EM, 230m water depth and ED, 310m water depth) in East Basin were used. We monitored oxygen and pH depth profiles with microsensors, porewater and sediment solid matter were analyzed for nutrient and metal contents. The total cell count was determined using DAPI. DNA was extracted from the sediment samples and 16S ribosomal RNA amplicons were analyzed with denaturing gradient gel electrophoresis (DGGE).

The cluster analysis performed on the DGGE fingerprint revealed that there is no distinct microbial community in the iron layer, instead the bacterial community of the iron layer was 97% similar to that of adjacent layers. The scanning electron microscope (SEM) images from the iron layer 10-12cm show filament like structures that was encrusted with spheres ca. 20 nm in diameter (Figure 1A,B).

Figure 1. SEM images of filament like structure in the iron layer (A). Filament or tube covered was with spheres (B).

Gallium in bauxite deposits
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Gallium is consumed in rapidly increasing amounts by high technology applications. The annual primary production of Ga in 2009 of 111t is set to increase twentyfold by 2030 [1,5]. However, Ga is the sixteenth most common element in the Earth’s crust (16ppm) and thus is much more common than metals like Cu, Zn, Ag or Cu. Despite of its relative abundance, Ga minerals are very rare and no distinct ore deposits from which gallium could be exploited as major product are known. This is attributed to the close geochemical affinity of Ga to Al resulting in Ga to substitute easily in rock-forming Al silicates (e.g., feldspar, nepheline).

Currently, almost all Ga is extracted as byproduct during beneficiation of bauxite. Ga occurs in bauxite in concentrations of <10-160ppm (Ø50ppm) [4, 5]. Based on the data of bauxite reserves and resources given by the USGS (2010) [5] and Bogatyrev & Zhukov (2009) [2] and under the assumption of an average Ga content of 50ppm, the geologically available Ga quantities in bauxites are estimated as 1.355Mt and between 2.75—3.75Mt Ga, respectively. The majority of bauxite deposits form by intensive chemical weathering of Al-rich lithologies During this process Ga behaves immobile much like Al, and is incorporated into Al-bearing minerals (e.g., gibbsite, kaolinite).


Crustal growth in the North China Craton at ~2.5 Ga: Evidence from in situ zircon U-Pb dating, Hf isotopes and whole-rock geochemistry of the Dengfeng complex
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The Dengfeng complex situated on the southern margin of the North China Craton (NCC) belongs to the southern portion of the Trans-North China Orogen. This late Neoarchean (~2.5 Ga) terrane is important to understand the formation and evolution of NCC during this period. The Dengfeng complex is well exposed in the Junzhao region and comprises two distinct lithologic units: supracrustal assemblage and plutonic rocks. LA-ICPMS magmatic zircon U–Pb dating shows that the complex formed within the range of 2547–2504 Ma. The available Hf isotope data indicate that the majority of ca. 2.5 Ga zircons from the Dengfeng complex give high εHf(t) values close to the initial Hf isotope ratios of the contemporaneous depleted mantle. These indicate that the rocks in the Dengfeng represent juvenile crust. The TTG gneisses in the Dengfeng complex display low Mg# (41-48), MgO (<2 wt%), Cr (6-14 ppm), Ni (9-22 ppm) contents and low Nb/Ta ratio (6-12), which are interpreted to have been produced by the partial melting of a flatly subducted slab. The metadiorites of the Dengfeng complex are typically characterized by high Mg# (59-69), MgO (3.5-6.6 wt %), Ni (82-130 ppm) and Cr (148-173 ppm) concentrations, and high LREE (LaN=38-487). Such geochemical features are similar to Archean sanukitoids. A two-stage model is applied here to explain the genesis of metadiorites of Dengfeng complex: (1) firstly, the mantle is metasomatized either by melts or by aqueous fluids from a subducted slab; (2) then, sanukitoid magmas were produced by partial melting of the hybridized mantle. Furthermore, the amphibolites of supracrustal rocks have a mixture of MORB- and arc-like geochemical affinities, suggesting the development of a back-arc in the southern part of the NCC at ca. 2.5 Ga. The contemporary late Neoarchean TTGs, sanukitoids and MORB-back arc association may represent a late Neoarchean tectonic mélangé, implying for a Neoarchean subduction-accretion process and the modern-style plate tectonics processes probably initiated in the southern NCC by 2.5 Ga.

Molecular iodine emission rates from *Laminaria digitata* as a function of algal part, irradiance and temperature

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Sea-to-air biogenic iodine fluxes play a key role in the global and local environmental iodine cycles, particularly in coastal areas where kelp beds are exposed to air during spring tides. The general knowledge of the marine sources and mechanisms of (elemental) iodine emission, either as molecular I\(_2\) or volatile iodo-carbons, is still very limited. Here time-resolved flux measurements of I\(_2\) emitted by the brown macroalga *Laminaria digitata*, probably the strongest iodine accumulator amongst living organisms, were achieved by applying incoherent-broadband cavity-enhanced absorption spectroscopy (IBBCEAS) [1,2]. I\(_2\) emission rates of three different (air-exposed) thallus parts of *L. digitata*, i.e. the distal blade, the meristematic area, and the stipe, were investigated under low-light and dark conditions [3]. Furthermore, impacts of light intensity and temperature on the I\(_2\) emission rates were investigated for blades. Overall I\(_2\) emissions were highly variable, but the release from stipes was ten times higher than that from meristematic areas and distal blades. Increased irradiances and temperatures resulted in higher I\(_2\) emissions, indicating the importance of I\(_2\) in algal stress responses. The results suggest that I\(_2\) emission may be considered an indicator of the physiological status of the alga, and that iodine might have a multifunctional role in *L. digitata*.


Computational studies of actinide clusters and hydrolysis reactions

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Advances in theory, algorithms, software, and computer architectures, have made it possible to begin to calculate reliably the thermodynamics for geochemical processes in solution. There is a need to develop a fundamental understanding of actinide-aggregate formation under conditions that promote hydrolysis. We are developing the scientific basis for a molecular-level understanding of nanaggregate species in terms of their structures, stabilities, formation reactions, and surface reactivities, particularly the formation of colloidal particles containing heavy elements. In addition, this research will help us to meet the need to develop new separations strategies for next generation nuclear fuels that are better able to remove stable metal aggregates without the need for extreme solution conditions. Our focus is on the initial aqueous reactions including olation and oxolation as well as the acidity of metal ions in solution. For the +2 metal aquo ions, it is possible to predict the size of the first solvation shell by predicting the correct pK\(_a\) in terms of experiment. Positive ions with a charge > +2 require more solvent shells in order to predict the pK\(_a\) reliably. We have studied a wide range of oxolaton and olation reactions of +2 cations and the type of reaction that dominates in terms of the thermodynamics is dependent on the cation size, the size of the first solvation shell, and the electronic structure of the ion. The structures of (ThO\(_2\))\(_n\) nanoclusters have been studied and compared to the analogous transition metal nanoclusters. Calculations of the hydrolysis reactions of the nanoclusters provide for the first time an estimate of the physisorption and dissociative chemisorption energies of H\(_2\)O on the ThO\(_2\) surface. The electronic structure of nanoparticles containing a Th\(_6\)O\(_8\) core will be discussed including predictions of particle acidity and proton location. These particles are of interest as they contain a Th\(_6\)O\(_8\) core embedded in an anion shell. There is good agreement between theory and experiment for the structures of the clusters.

This work is supported by the U.S. DOE, OBES, Chemical Sciences under contract DE-AC02-06CH11357.
Speed limits to soil weathering and CO₂ withdrawal

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Weathering fluxes in soil-mantled landscapes are capped by a global maximum that has important implications for Earth’s long term climate. We identify the empirical, statistical and theoretical limits to climate, weathering and uplift feedbacks using a new global compilation of long term, soil-based denudation and weathering rates from cosmogenic nuclides and short term, river-based sediment and dissolved loads. Weathering accelerates by the increased exposure of minerals to erosion, and recently it was suggested that 50% of the global CO₂ withdrawal occurs in the world’s active mountain belts [1]. The observation that chemical weathering rates and physical erosion rates are tightly correlated has vindicated this hypothesis. But this relationship is predominantly valid for soil-mantled landscapes, and not rapidly uplifting mountain belts [2]. Erosion rates may far exceed the soil speed limit, and are typically associated with landscapes of high relief and hillslope gradients [2]. There, erosion is governed by mass wasting processes typical of non-soil-covered landscapes in active mountains [3]. Yet chemical weathering rates from dissolved loads of rapidly eroding mountain rivers suggest that these landscapes also obey or fall below the limit of weathering observed for soils. Considering that such mountain belts are a small component of the continental land surface, we quantify that even if weathering fluxes in such areas were higher than today, they would represent a minor contribution to global CO₂ withdrawal. Therefore, Earth’s long term climate sees little drawdown and more drawbacks from uplifting areas where denudation drives above the soil speed limit.


Why do earthworms synthesize ACC?

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From the early work by Darwin [1] several hypotheses have been proposed to answer this question, namely pH buffering of the blood and the ingested plant material, respiratory functions, egg formation or simply spurious mineralization.

In this study we investigated the microstructural transformations which take place during the carbonate formation inside the calciferous gland of the earthworm species Lumbricus friendi Cognetti. We firstly identified the presence of ACC [2] by FTIR and then we followed the different evolution stages of calcium carbonate in the precursor fluid previous to the formation of to the solid phases by performing in situ XRD experiments.

Figure 1. Two transformation stages from ACC to crystalline phases in earthworm’s spherulites.

The results presented here shown that the formation of crystalline polymorphs of calcium carbonate in earthworms is preceded by the precipitation of ACC in a process that seems to follow a truly biomineralization mechanism, controlled by the organism. The high solubility is beneficial for temporal storage of calcium carbonate ions which could then get dissolved and used elsewhere according to the organism’s requirements. Stabilisation of ACC seems to be achieved thanks to the presence of macromolecular constituents in the organic matrix, which also could be selectively used to promote the elimination of carbonate excess by nuclei induction of the crystalline phases and thus providing an efficient mechanism for Ca²⁺ control in the intracellular fluids.

Toxicity of silver nanoparticles to environmental microbial consortia

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Nanomaterials, particularly silver nanoparticles (AgNPs), are present in a large number of consumer goods due to their strong antimicrobial properties. Their extensive use raises concerns as to their release to the environment and their potential toxicity to aquatic microbiota.

The mechanism of AgNPs toxicity remains elusive and may include direct inhibition by the nanoparticulate form and/or indirect toxicity via soluble silver released from AgNPs. Additionally, numerous studies have attempted to unravel the role of AgNP size and coating in bacterial toxicity response but there remains a large gap in our understanding of the impact of basic AgNP characteristics on their toxicity.

Here we report on a systematic study of AgNP toxicity towards two pure cultures -Escherichia coli and Bacillus subtilis- and a microbial community from lake Geneva. We studied the effect of size (5nm, 10nm, 20nm, 50nm and 100nm) and that of surface coating (polyvinylpyrrolidone, tannic acid, citric acid and carbonate) on toxicity.

The AgNPs were obtained commercially and extensively characterized by electron microscopy (EM), dynamic light scattering, zeta potential and the release of silver ions quantified by inductively coupled plasma mass spectrometry. The impact of AgNPs (0 to 1mg/L) on growth was monitored by optical density at 600nm, by colony formation for pure cultures and by measuring protein concentration and monitoring the microbial diversity of the community for the consortia. Additionally, the spatial relationship of AgNPs and cells was assayed by EM imaging of resin-embedded cells. The environmental relevance of the experimental conditions was ensured by growing cultures in artificial lake water.

Results to date show little toxicity to laboratory strains with E. coli being more sensitive than B. subtilis and size being a less important factor than surface coating. The systematic approach of this study –where AgNP size distribution is narrow and the geochemical conditions and microorganisms environmentally relevant- may be helpful to policy makers aiming at regulating the use of AgNPs in consumer goods.

VESPER XRF and Laue Diffraction mapping of Carlin-type auriferous arsenian pyrite

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Carlin-type gold deposits produce 8% of the world gold, and the main ore is auriferous pyrite commonly associated with various trace elements (Ag, As, Au, Cu, Hg, Ni, Sb, Se, Te, Tl and Zn). Their compositions have been investigated using electron-microprobe (EMP) and dynamic Secondary Ion Mass Spectrometry (SIMS), which indicates that gold and related trace elements occur in complex, micrometer-size irregular zones or overgrowths within single grains. The development of VESPER (Very powerful Elemental and Structural Probe Employing Radiation from a Synchrotron) allows for non-destructive elemental mapping and crystal structure determination through XRF and Laue diffraction (LD). This methodology was applied in selected auriferous pyrite grains that were previously investigated using EMP and SIMS to advance our understanding of the relationship between the abundance of trace-elements and crystal structure.

The VESPER elemental mapping results are consistent with those obtained by SIMS and EMP; however it offers the advantage of mapping a wide range of elements and the collection of LD patterns simultaneously and non-destructively. The elements that have adequate peak resolutions are Au (L series) and As, S, Fe, Ni, Cu (K series). Elements with peak overlap that have not yet been resolved include Ag, Sb, Te, Tl and Zn. Synchrotron LD data was collected along selected domains and the crystal structures are being interpreted.
**Fluids nature at peak of ultrahigh-pressure metamorphism in deep subduction zones – Evidence from diamonds**

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Role of fluid circulating in deep subduction channels was a subject of many outstanding geochemical and numerical modelling studies. One of the intriguing processes is a fluid-rock interaction during subduction of the continental slab because the latter is characterized by contrast chemistry in comparison with the surrounding mantle and its fluids. Diamond due to its chemical inertness is the only mineral which contains “unchanged” fluids that was trapped during its crystallization at the peak of UHP metamorphism. We have demonstrated earlier with FIB-TEM studies that many diamonds from the UHPM terranes of Kazakhstan and Germany preserved intact C-O-H fluid inclusions [1]. This fluid responsible for diamond crystallization contains traces of both crustal and mantle components: Al, K, Ca, Mg, Fe, Si, Ti, V, Zn, Co, Fe F, Cl, S [1]. We have recently found more evidence to support crust-mantle origin of the fluids penetrating continental slabs in the deep subduction channels. This derives from a new finding of the polycrystalline diamonds included in zircons from Erzgebirge feldspathic gneisses containing remnants of fluid available for their compositional evaluation with EDAX spectrometry. The diamonds consist of 5-15 crystals of 0.3-5 micron size with a typical “zig-zag” grain boundaries and triangle voids filled with a C-O-H fluid with traces of Al, Ca, V, Zn, S, Si, Mg, Fe K in different combination. Such observations emphasize that diamonds from UHPM terranes have a similar nature of crystallization – from a fluid originated from a mixed crust-mantle geochemical reservoir. Moreover, the Kokchetav diamonds 3He/4He ratios are similar to those known for OIB setting [2].


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**Kinetics of the reaction perovskite + ferropericlase = ringwoodite**

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The kinetics of solid-state disproportionation reactions can be strongly asymmetric due to the different diffusive length scales of disproportionation versus recombination. Transport of material from the lower mantle into the transition zone requires the reaction of perovskite (pv) plus ferropericlase (fp) to produce ringwoodite (rw); this reaction is diffusive on the grain-length scale and hence might allow a significantly wide region where metastable phases exist. We present experiments to investigate the kinetics of this reaction. We have assumed that the transformation from pv to majorite (mj) is fast (being diffusive at the unit-cell length scale) and hence performed coupled reaction experiments of MgO with (Mg,Al)(Al,Si)O3 at a pressure of 20 GPa (in the rw and mj stability fields) at temperatures of 1773 to 2123 K. The reaction is, as expected, mediated by diffusion of chemical components through the growing rw layer, with growth rate of the layer being linear with t². rw grows with strong topotactic relations to the MgO which would, on completion of the reaction, result in single (or twinned) crystals of rw replacing the MgO grains. However, the kinetics of the reaction is further complicated by the incompatibility of aluminium in rw. As the rw layer grows, a double-diffusive instability develops with the rw-mj interface becoming fingered to maximise the surface area from which to diffuse aluminium into the garnet. The mean grain-size of regions with this texture is ~2 micrometres, which shows little coarsening due to zener pinning. Reaction continues until all of the MgO is replaced leaving fine-grained reaction rims between these rw regions and the remaining excess (Mg,Al)(Al,Si)O3, garnet. Two ways to estimate the grain size of the lower mantle might arise from this:

1. Seismological estimates of the thickness of the 670-km discontinuity are consistent with the equilibrium reaction. This means that the width of the region where the metastable mj + fp = rw reaction occurs is below seismological resolution.

2. The reaction texture might (occasionally) survive in porphyroclastic mantle xenoliths.

Both these estimates are consistent with a maximum lower-mantle grain size of about 1 cm.
Mid and heavy REE in carbonatites at Lofdal, Namibia

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Carbonatites provide most of the World’s rare earth elements (REE) but are characteristically enriched in the light REE with low contents of the more highly sought after mid and heavy REE. The Lofdal carbonatite complex, 35 km NW of Khorixas, Namibia, is an exception in that it contains hundreds of carbonatite dykes, some of which are mid and heavy REE-enriched, containing up to 3% xenotime-(Y) in dolomite-ankerite and ferruginous calcite carbonatite. Gd and Dy are the most abundant lanthanides in the xenotime-(Y).

ThO2 content is the main environmental problem with REE deposits and at Lofdal, there is up to 1 wt% ThO2 in magmatic xenotime-(Y) and usually lower, about 0.3 wt%ThO2, in hydrothermal xenotime-(Y). However, many rocks contain Th silicate. The hydrothermal xenotime-(Y) occurs in shear zones and associated calcite has a high 48Sr46Sr ratio of 0.70804, δ13C (‰V-PDB) of -3.66 and δ18O (‰V-SMOW) =18. The xenotime-(Y) at Lofdal is the same age as the main carbonatite (765 ±16 Ma) and thus later metamorphic alteration can be ruled out. However, together with the presence of xenotime-(Y) in albitted country rocks and carbonatite-free shear zones, there is good evidence that most of the xenotime-(Y) formed from a carbonatite-related hydrothermal system circulating around the dykes.

Magmatic processes during the formation of Monte dei Porri Volcano, Island of Salina, Aeolian Islands, Italy


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The island of Salina is the second largest of the Aeolian Islands, the subaerial expression of the Aeolian Magmatic Arc, located in the Tyrrhenian Sea, southern Italy. Salina lies in the centre of the arc and exhibits the widest variation in geochemical composition across all the Aeolian Islands, ranging from high-alumina basaltic to dacitic lava flows to rhyolitic pumiceous tephras erupted from 6 volcanic centres.

The Monte dei Porri volcanic eruptions were the last cone building events on the island occurring between 67ka and 13ka and occurred after 60ka of repose. The units consist of basaltic-andesite to dacite lavas, interlayered with unconsolidated tephras consisting of juvenile scoria fragments, entrained lithics and rhyolitic pumices. Phenocryst assemblages consist of calcic plagioclase (often with oscillatory zoning), clinopyroxene (augite), olivine and titanium-iron oxides ± orthopyroxene (often zoned), K-feldspar and quartz. Melt inclusions are a ubiquitous feature of all units and appear to be recrystallized in the lavas and occur as both recrystallized and glassy inclusions with and without vapour bubbles in the tephras. Rare primary fluid inclusion assemblages are also present in the tephras.

Raman spectroscopy of the glassy melt inclusions of the tephras reveals the presence of volatiles in the melt inclusion glass in the form of H2O. CO2 was not found in the glass or the vapour bubbles. Geothermometry based on plagioclase-liquid and clinopyroxene-liquid models indicates crystallisation temperatures of ~1200°C for feldspars and ~1050°C for clinopyroxene phenocrysts. Petrographic analysis suggests the mixing of one or more magmas with different compositions played an important role in the evolution of the magmatic system.
A predictive thermodynamic model for element partitioning between plagioclase and melt

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There are various attempts in the literature to infer from the chemical zoning in plagioclase phenocrysts the magma evolution [1] and to determine magma residence times of plagioclases from diffusion modelling [2]. Both methods rely on accurate knowledge of partitioning coefficients between plagioclase and melt, $D_i$, and their dependencies on thermodynamic parameters and chemical composition. Based on a regular mixing model and numerical fitting of numerous experimental data [3] derived an equation for Sr and Ba of the form,

$$RT \ln D_i = A_i X_{An} + B_i.$$

In a more recent work [4] the same relation was also used for various other elements to fit experimental pl-melt partitioning data. However, there is no a priori justification to use this relation also for other elements than Ba and Sr.

Here we present a new predictive model for the element partitioning between the metal site in plagioclase and melt. We have used the Brice model [5] to fit simultaneously the experimental data of 115 partitioning experiments, including those of [4] and unpublished data (partially published in [5]). The dependency of $D_i$ on $X_{An}$ is dominated by lattice strain effects and is related to the linear dependence of the optimum ionic radius $r_0$ on the anorthite content. Once the relevant parameters of the Brice model, $r_0$ and the Young’s modulus of the site, are calibrated, the partitioning data can be corrected to isolate their $T$ dependence. The inferred $T$ dependence of the divalent cations and monovalent cations is perfectly consistent with available data for the free energy of fusion for anorthite and albite, respectively. The effect of the melt chemistry cannot be ignored in general but is minor compared to the lattice strain effects in most cases.

The major implication of this new model is that $D_i$ becomes less sensitive to $X_{An}$ and more sensitive to $T$ than predicted by the relations of, e.g., [3] and [4]. This can be explained by the implicit relationship of $X_{An}$ and $T$ in most partitioning experiments.


Sr-Nd-Hf-Pb isotope systematics of the Oyu Tolgoi Cu-Au deposit (Mongolia)

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New Sr-Nd, Hf and Pb isotope data are presented for a representative suite of 21 samples of plutonic and volcanic rocks (D3 to C1) from the giant Oyu Tolgoi porphyry Cu-Au district in the South Gobi, Mongolia.

Sr-Nd isotopes (whole-rock) show a restricted range of initial compositions, with $\epsilon$Nd varying from +2.1 to +7.4 and $(\frac{87}{86})$Sr$(\frac{87}{86})$ predominantly between 0.7035 and 0.7045 reflecting formation from a relatively uniform juvenile lithophile-depleted source.

Hf isotopes (zircon) exhibit a range of -4.5 to +13.6 (Fig. 1). Felsic rocks show predominantly (apart from one sample) a juvenile mantle-derived signature whereas volcanic rocks exhibit some mixing with evolved crustal sources.

Pb isotopes (whole-rock) indicate a rather preserved array of isotopic compositions such as $^{208}$Pb/$^{204}$Pb 17.773-19.058, $^{207}$Pb/$^{204}$Pb 15.445-15.544 and $^{206}$Pb/$^{204}$Pb 37.456-38.489. These are in full agreement with Sr-Nd-Hf isotopes indicating presence of a mantle component. Several samples show contributions from a MORB-related source.

All four isotopic systems hint that magmas from which the large Oyu Tolgoi porphyry system was generated, originated predominantly from juvenile material within the subduction-related setting of the Gurvan-Saikhan terrane.

Figure 1: Hf and Nd isotopes for the Oyu Tolgoi deposit.
Biogeochemical sustainability of semi-natural ecosystem

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The research is based on the novelty balance approach to the migration of artificial matter between biotic levels of an ecosystem and inanimate matter. The Geochemical transition factor (GTF) that represents the quantity of substance accumulated by plants from the area unit has been utilized for balance calculations. The temporal dynamics of GTF, permitting to assess the intensity of biogeochemical flux, suggested as volume of substance transferring during the time unit through the area unit of conditioned interface between abiotic and biotic levels.

In meadow ecosystem the only $10^{-5} - 10^{-3}$ part of artificial contaminants is involved to biogeochemical cycling. The considerably greater part accumulates in living matter of forest ecosystem: up to 50% of $^{14}$C (Fig. 1), 10% of $^3$H, 20% of $^{90}$Sr, 13% of $^{137}$Cs, 3% of $^{241}$Am, 6% of $^{90}$Zn, 1% of Al and Ni, and less than 1% of Fe, Mn, and Cu. Artificial radionuclides and heavy metals are strongly accumulated in bottom deposits of aqueous ecosystem: anomalies of contamination are closely localized to the pollution source. Accumulation of $^{14}$C by micelium from irradiated graphite is 50-100 times less than from sucrose solution in check experiment.

Figure 1. Distribution of Carbon isotopes in pine ecosystem

The insignificant part of artificial matter involved to biogeochemical cycling determines the environmental capacity to contamination. Experience of geoecological investigations gives rise to conclusion about comparative sustainability of ecosystems in spite of the catastrophic increase of artificial loading.

Compact representation of complex organic aerosol processes

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Myriad organic compounds constitute organic aerosol (OA), tightly interconnecting multiphase chemistry, phase partitioning equilibria, and mass-transfer dynamics. Representations range from bare-minimum simplicity (e.g. omitting 12.5% of all terpenes as non-volatile, non-reactive, water-soluble organic aerosol) to maximal complexity (explicitly representing the multiphase chemistry and phase partitioning of millions of compounds). We favor a middle ground, grouping organic compounds in a property-based space that is directly tied to both vial physical properties as well as observable characteristics of ambient and lab-generated organic particles. This is the volatility basis set.

The first incarnation followed a single property – volatility – expressed in terms of a saturation mass concentration and typically lumping compounds into bins separated by factors of 10 in a logarithmic space. The 1D-VBS can precisely describe ideal phase partitioning over as many orders of magnitude as the number of bins. It can thus span the complete range of volatility relevant to atmospheric organics with 9 or so model compounds. It can also be used to fit chamber and dilution data to empirically constrain the volatility distribution of complex processes. It fosters insight into chemical evolution by forcing a mass balance. However, the single dimension suffers when confronted with non-ideal solutions as well as complex chemistry.

We have now added a second dimension, representing the oxidation of organics, to form a 2D-VBS. Oxidation state of bulk aerosol can be directly measured with advanced mass spectroscopy, and of course individual molecules can be located in this space as well. Oxidation in the atmosphere is irreversible, while volatility goes through a minimum as oxidation progresses. These fundamental behaviors are readily captured in the 2D-VBS.

As an illustration and test of OA evolution, a large team conducted the Multiple Chamber Aerosol Chemical Aging Study (MUCHACHAS) in 2008-2010 to observe the effects of OH radical “aging” on biogenic secondary organic aerosol (SOA). The effects were dramatic. They varied in different chambers, but a 2D-VBS model of the chemistry and chamber characteristics captures this variation using a predictive, previously published description of OA aging chemistry, showing that OA mass can double with aging. This aging chemistry must be included in transport models.
Copper and zinc isotope composition of China and India dust sources

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Copper (Cu) and zinc (Zn) play key roles in aquatic ecosystems. Zinc is an essential trace element limiting the biological productivity in the open ocean and Cu is potentially toxic to phytoplankton. Work to date suggests that the stable isotope systems of these metals can improve our understanding of their aqueous chemistry and behaviour in the marine environment. Significant spatial variability in isotopic ratios was found between and within ocean basins.

At present, one of the major gaps in knowledge is the characteristics of the isotopic composition of Zn and Cu of terrestrial sources into the marine ecosystem, in particular atmospheric deposition, which is the major source of trace elements to the remote open ocean.

Here we present the first characteristics of the Cu and Zn isotope compositions of the major dust sources in China and India, and discuss the findings with respect to (i) the dominant controls (mineralogy size fractions and Enrichment Factor), and (ii) their implication for the application to marine studies, focussing on the North East Pacific Ocean (NEPO).

a) We observe significant Cu and Zn isotopic variations between bulk samples from Chinese dust, Chinese Loess, and Indian dust (error in 2SD), i.e., Chinese deserts (Taklamakan, Badain Jaran, and Tengger): \( \delta^{65}{\text{Cu}}_{\text{NIST976}} = 0.06 \pm 0.11 \text{%} \) (n=10), \( \delta^{66}{\text{Zn}}_{\text{py}} = 0.19 \pm 0.19 \text{%} \) (n=10); Chinese loess: \( \delta^{65}{\text{Cu}}_{\text{NIST976}} = 0.27 \pm 0.19 \text{%} \) (n=12), \( \delta^{66}{\text{Zn}}_{\text{py}} = 0.41 \pm 0.17 \text{%} \) (n=15); Thar Desert (India): \( \delta^{65}{\text{Cu}}_{\text{NIST976}} = 0.48 \pm 0.12 \text{%} \) (n=4), \( \delta^{66}{\text{Zn}}_{\text{py}} = 0.49 \pm 0.22 \text{%} \) (n=5). b) Cu isotope values seem to be negatively correlated with the abundance of the clay mineral illite at 95% CI R² = 0.74, (n=10). c) The \( \delta^{65}{\text{Cu}}_{\text{NIST976}} \) and \( \delta^{66}{\text{Zn}}_{\text{py}} \) values differ among the various size fractions of Chinese deserts by up to 0.97 ‰ (Tengger Desert) and 0.35 ‰ (Taklamakan Desert), respectively. This implies that bulk isotopic signatures might be misleading for the characterization of dust. d) Enrichment factors (EF) of the dust range between 0.48 (Thar Desert) and 1.86 (Taklamakan Desert) for Cu and between 0.40 (Chinese loess) and 0.70 (Tengger Desert) for Zn, suggesting that the lower EF values, the heavier the isotope signature of the dust. e) The isotope signature of long range transport Chinese dust (≤5 μm) input to the NEPO area has values of \( \delta^{65}{\text{Cu}}_{\text{NIST976}} = 0.16 \pm 0.19 \text{%} \) and \( \delta^{66}{\text{Zn}}_{\text{py}} = 0.29 \pm 0.24 \text{%} \), which are lower for Cu and similar of Zn relative to the isotope signatures of dust input estimated in pervious studied of NEPO surface waters.

Multiple magma inputs and sulfur sources in the development of the BIC intrusion, Northern Michigan, Midcontinent Rift system

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The BIC intrusion is located in the Marquette-Baraga dike swarm in the Upper Peninsula of Michigan, and is associated with magmatism related to the development of the ~1.1Ga Midcontinent Rift System. The intrusion is currently being evaluated for the presence of economically viable sulfide-rich Ni- Cu-(PGE) mineralization. Rio Tinto’s Eagle deposit is located 43 km to the west within the same dike system; the geometric form of the BIC intrusion, however, is distinctly different from those of the intrusions found in the vicinity of the Eagle deposit. The BIC intrusion is funnel-shaped with basal peridotite overain by clinopyroxenite and gabbro. Sulfide minerals (pyrrhotite, chalcopyrite, pentlandite) are found in all of the units units but massive sulfide mineralization is restricted to the base of the peridotite unit. Country rocks are composed of siltstones and shales that are sulfide-bearing themselves. A smaller satellite intrusion is referred to as Little BIC, which is composed of peridotites with both massive and semi-massive (net-textured) mineralization.

Sulfide distribution in the BIC intrusion is variable, suggesting that multiple pulses of sulfide-saturated magma were involved in its genesis. \( \delta^{34}\text{S} \) values of sulfide minerals throughout the intrusion fall within a narrow range of -2 to +2‰. \( \delta^{34}\text{S} \) values of the sedimentary country rocks show a much wider range of -6 to +20‰. The massive sulphides in Little BIC have the same narrow range of \( \delta^{34}\text{S} \) values as in BIC, but semi-massive sulphides are considerably higher (~+6‰) and clearly signify a large component of crustally derived sulfur. The BIC system conforms to a growing body of evidence for the importance of multiple sulfur sources in conduit-related Ni-Cu-(PGE) occurrences. We are currently evaluating the possibility that different processes for the attainment of sulfide saturation (e.g. fractional crystallization versus sulfur assimilation) are responsible for the sharp difference in \( \delta^{34}\text{S} \) values between semi-massive sulfides at Little BIC and other sulfide occurrences in the system.
Do fluid inclusions preserve their initial composition? Experimental studies of H$_2$O diffusion through quartz

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The main focus of our diffusion studies lies on experimental works on synthetic and natural fluid inclusions (FI) in well selected quartz crystals. A major point of our investigations is to perform re-equilibration experiments with synthetic FI which are composed of water-related species, such as H$_2$O, D$_2$O and H$_2^{18}$O, at known P-T conditions and specific molar volumes of the liquid phase. Due to the possibility of post-entrapment compositional and density changes of FI, the analyses of fluid properties have to be performed with particular attention. To comply with this requirement we work on molecules with different properties, e.g. different melting points of H$_2$O and D$_2$O (melting points: 0 °C H$_2$O vs. +3.8 °C D$_2$O) to achieve better quantitative insights on the diffusion rates. Re-equilibration experiments are carried out at high experimental temperatures and pressures (max. 700 °C and 1 GPa). We design our recent experimental work to test the behaviour of aqueous FI in quartz under conditions of different pressure and different water fugacity. We expect a movement of the water-related species within the quartz lattice. Re-equilibration processes are not yet fully understood, therefore further investigations are required to characterize all aspects of post-entrapment changes in FI. Additionally we are able to determine changes in the shape of the synthesised inclusions (morphological changes) interrelated with the location (depth) of the inclusions within the quartz crystal. First results lead to the assumption that the size, the shape (Fig. 1) and the location directly correlate. This unambiguously correlates with the measured changes in the fluid-phases composition of the primary synthesised FI.

Figure 1: Photomicrograph of a FI in quartz after 19 days of re-equilibration. Pressure: 337 MPa; Temperature: 600 °C (left), 400 °C (right).

Host rocks of Santa Eulália Plutonic Complex (Southern Portugal): A preliminary study

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The Santa Eulália Plutonic Complex (SEPC) is a calcalkaline granitic body that occupies an area of 400 km$^2$ and is located in the Variscan Iberian sector. SEPC is considered as late-Variscan because it cross-cuts the regional variscan structures, namely a major NW-SE shear zone in the contact between the two axial geotectonic zones of the iberian varican belt. The host rocks of the plutonic complex are composed by metamorphic formations from Upper Proterozoic to Lower Paleozoic. In the NE-sector of the shear zone a metasedimentary Ediacaran unit (Série Negra) outcrops, composed by metasedimentary siliciclastic rocks, including some black cherts. In the SW-sector of the shear zone, a low-grade metasedimentary and metavolcanic unit involving quartz-pelitic, carbonated and volcanic rocks, correspond to the Early Cambrian sequence.

In the western sector of SEPC, several metasedimentary enclaves are present mainly with pelitic and carbonated composition. These enclaves show internal structure and lithological diversity consistent with the external metasedimentary units and, due to the thermal effect, have intense metamorphic recrystallization. One of the enclaves near the NW border of SEPC, marble, calc-silicated rocks and acid porphyritic rocks were studied, including petrography, mineral and whole-rock chemistry. The calc-silicated and the porphyritic rocks show similar Eu-normaly, Eu/Eu* respectively 0.86 and 0.88. However, the fractionation of LREE and HREE is quite different: in porphyritic rocks (La/Sm)$_n$ = 6.59, (Gd/Yb)$_n$ = 2.13, while in calc-silicated rocks (La/Sm)$_n$ = 1.66, (Gd/Yb)$_n$ = 1.38, (La/Yb)$_n$ =3.04 and (La/Yb)$_n$ = 181.63. The marble has a higher negative Eu-anomaly, with Eu/Eu*=0.57 and (La/Sm)$_n$ = 3.15, (Gd/Yb)$_n$ = 1.62, (La/Yb)$_n$ =7.87 and (La/Yb)$_n$ = 17.31. These preliminary geochemical data indicate that all these lithologies derived from a continental crustal source.

This work has been financially supported by PTDC/CTE-GIX/099447/2008 (FCT-Portugal, COMPETE/FEDER).
Synoptic approaches to scale CH₄ flux in boreal landscapes

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Boreal wetlands are an important source of atmospheric methane (CH₄) and susceptible to future climate change. Typically, boreal wetlands form microtopes embedded in complex landscapes, posing a challenge to scaling CH₄ source strength to greater areas. Here we report on an analysis of air borne (LiDAR, hyperspectral scanning) and ground based (chamber measurements, molecular analysis) approaches to characterize and scale CH₄ fluxes in a highly stratified mountainous landscape in Southern Norway (60°22' N 9°39'E, 510-750 m, 3°C, 850 mm). We investigated relationships between peat depth, porewater CH₄ concentrations and CH₄ emission fluxes and found a significant correlation between CH₄ pore water concentration and VNIR reflectance spectra. Spectral separation was further tested in predefined vegetation/wetland types. We used molecular markers and in vitro CH₄ uptake kinetics to infer the abundance and activity of type I and type II methanotrophs in different landscape units. Synoptic approaches to scale CH₄ flux in heterogeneous landscape by means of molecular and biophysical signatures will be discussed.

Investigation of the precision and accuracy of isotope ratio measurements for atmospheric sampling for laser ablation multi collector-ICPMS

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Laser ablation ICPMS is a powerful method for solid sample measurements. The sample size is however limited by the ablation cell size. Many efforts were made in developing ablation cells with different volumes and shapes for large samples. However the coupling of a gas exchange device (GED) [1] to the ICPMS allows to get rid of the ablation cell. The laser ablation process takes place in air environment. The aerosol is sucked into the GED by a membrane pump through a tube located directly at the ablation site. In the GED, the air is exchanged to Argon. The aerosol is then transported to the ICP in an Argon atmosphere. The figures of merit for atmospheric laser ablation were determined and similar accuracies as for conventional laser ablation were reported [2].

Laser ablation coupled to a multi collector-ICPMS (MC-ICPMS) allows precise isotopic information of a sample, used for e.g. age determination. These samples are mostly archeological and do not always fit into an ablation cell. The isotope ratio determination with LA-GED-MC-ICPMS would therefore be a method of choice for large and precious samples.

The precision and the accuracy of the atmospheric sampling for isotope ratio measurements were investigated with a Ti-Sapphire based femtosecond laser (Legend, Coherent Inc., Santa Clara (CA), USA) coupled to a gas exchange device and a Nu Plasma (Nu Instruments, Wrexham, UK). The measurements were done on pure lead, galena, brass and zircon. Even if a loss in sensitivity is observed, similar precision and accuracy were obtained comparing the atmospheric ablation with the conventional laser ablation set up.

**Inception! Quantifying U-series disequilibria during the early stages of granite alteration**

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Quantifying the balance between soil production from saprolite and regolith production from bedrock is crucial to assessing soil sustainability over human timescales, quantifying how landscapes evolve over millenia, and understanding weathering-related feedbacks in Earth’s long-term climate evolution. Uranium-series isotopes have recently emerged as a tool for constraining rates of soil production from saprolite and regolith production from bedrock (e.g. [1-4]). To date, U-series work on weathering has focused mostly on samples in which the inception of weathering occurred at depth beneath a mantle of similarly weathered material. In this work, we focus on a bare rock ridge, using U-series isotopes to constrain weathering rates during the early stages of granite alteration. The goal is improved understanding of the pronounced dicotomy of bare and soil mantled rock on the slopes of the Sierra Nevada Batholith (California). Cores ~30cm long were drilled in a granitic ridge: one core was collected under a thin regolith cover, probably wind-blown material, in a small depression and shows evidences of relatively extensive weathering. This core is of special interest for addressing the role of a regolith cover in promoting weathering of the underlying bedrock. Another core was collected in nearby almost pristine bedrock but showing some evidences of weathering. Uranium and thorium isotope composition of samples taken along these cores will shed light on the mobility of chemical elements and the rates of granite weathering during the early stages of water-rock interaction.


**Contrasting mantle signatures along the Mid-Atlantic Ridge (10-50°N)**

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The description of mantle geochemical heterogeneities contributes to the understanding of time and length scales of mantle convection. Using trace element and Sr-Nd-Pb isotopic ratios, the geochemical structure of the northern mid-Atlantic ridge between 10 and 50°N has long been described with major anomalous zones at the latitudes of 14°-15°N, 38-39°N and 42-43°N. New Hf isotopic data from basaltic samples along this 10-50°N section of the ridge (shown as solid symbols in figure below, open symbols indicate published values) combined with Sr or Nd isotopes reveal clear contrasting geochemical signatures of different sections of the ridge. It emphasizes the heterogeneous character of the depleted mantle source of MORB, as previously reported and discussed with Sr isotopes in [1] and brings a new perspective on the mantle dynamics in the region.

Os isotope and PGE data on the age and evolution of lithospheric mantle in the central Siberian craton

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The Siberian craton was assembled 1.8-2.1 Ga ago from terrains containing components as old as 2.4-3.5 Ga [1]. To better constrain the age of the lithospheric mantle in the central craton and its relationship to the events that formed or assembled the overlying crust, we present new whole-rock Re-Os and PGE data on 31 fresh (LOI <1%) spinel and garnet peridotite xenoliths from the Udachnaya kimberlite [2]. 18 out of 24 refractory (0.1-1.2% Al2O3) rocks in this study contain 1-10 ppb Os. They mostly yield TRD ages from 1.5 to 2.3 Ga (average 1.8 Ga). The TRD ages do not correlate with P-T estimates (<2.5-6.8 GPa; 760-1330°C), hence depth. These peridotites are depleted in Pd, less commonly in Pt relative to Os-Ir-Ru, with the strongest Pt-Pd depletions in cpx-free spinel peridotites, likely reflecting the lower compatibility of Pt and Pd in residues of melting. Six refractory peridotites have low Os (<0.5 ppb), high Re/Os and yield low (0.7-1.6 Ga) or meaningless TRD ages. Cpx- and gar-rich peridotites (1.4-4.0% Al2O3; likely re-fertilised) with Os >1 ppb have eruption-age-corrected 187Os/188Os = 0.120-0.124; some show high Pt/Ir and Pd/Ir indicating Pt-Pd mobility during melt metasomatism.

Overall, Re-Os ages in Udachnaya peridotites are Paleoproterozoic (including 7 out of 8 samples from earlier work [3]), coeval with final rather than early stages of craton formation. Older ages have been reported on megacrystalline dunites (3 out of 5 in [3]), eclogites [4] or inclusions in diamonds [5] that cannot be abundant in the mantle. Thus, long-lived, thick, cold, diamond-bearing lithospheric keels may be generated in the Proterozoic as well as in the Archean.


Permafrost active layer dynamics inferred from major element geochemical signatures in six Arctic Alaskan rivers

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Arctic climate warming is expected to degrade permafrost and affect watershed hydrogeology and biogeochemistry. Increasing temperatures could lead to the downward migration of the seasonally thawed (active) layer into previously frozen soil. This could create a unique weathering signal in surface waters during late summer and early fall when the active layer is at its deepest extent. The response of permafrost to climate warming may not lead to a simple, homogeneous increase in active layer depths. Ice lenses, peat layers, and heterogeneous soil ice (water) contents will respond differently to warming. Our study was initiated to determine whether geochemical tracers can provide a proxy for these active layer dynamics in Arctic watersheds.

We collected up to 65 surface water samples from six Arctic Alaskan rivers from melt to freeze-up in 2009 and 2010. Watershed areas range from 1.6 to 610 km2. Two rivers were underlain by organic rich permafrost, two rivers drained mountainous bedrock, and two rivers were underlain by both bedrock and organic rich permafrost.

We measured the major ion geochemistry of the water samples. For most of the rivers, Na, Ca, Mg, and SO4 concentrations are lower during melt runoff and steadily increase throughout the summer into the fall. Nitrate concentrations increase steadily in the late fall in bedrock dominated streams, suggesting a decrease in N assimilation rates in the bedrock soils during late summer and fall. Our results suggest river chemistry is driven by flow paths that deepen from surface to mineral soils as the melt season progresses.
Comparative planetology – What are the factors controlling the nature of terrestrial planetary crusts?

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Size, composition, or location?

Within the Solar System, rocky bodies (planets, moons, asteroids) have a variety of sizes and crustal compositions. A common view is that “there are more variables than planets” [1], whereas others insist that the only significant factor controlling planetary evolution is the size of the body [2]. Consideration of pairs of similar sized planetary bodies (e.g., Earth/Venus; Moon/Mercury; Moon/Io, Callisto/Ganymede) suggests that two other factors are also important.

Firstly, the composition of the body controls much of its evolution, including the nature of its crust (both primary and present-day). Whether the mantle of the body is Fe-rich (e.g., Moon, Mars) or Mg-rich (Earth, Venus, Mercury) controls the compositions of erupted basalts but, more importantly, can lead to plagiodolite flotation in a magma ocean under anhydrous conditions. Presence of volatiles, particularly water, to the mantle inhibits formation of an anorthositic crust [3]. Water also lowers the solidus of basalts, which can then partially melt to produce magmas of intermediate compositions which are too buoyant to subduct, leading to formation of a silicic continental-type crust. Significantly, this process does not require the operation of plate tectonics but only requires the melting of hydrated basaltic material, as is demonstrated by the Archean TTG crust of the Earth.

Secondly, the location of the planetary body is an important factor, as seen in the dichotomy between Ganymede and Callisto in which the proximity to Jupiter governed the amount of impact-related heating [4] and later tidal heating, or in the contrasting magmatic histories of the Moon and Io.

Based on the three main factors, predictions can be made regarding the nature of crusts that are likely to be formed on planetary bodies of different sizes and bulk compositions, and this can then be extended to a consideration of specific locations of planets or moons (e.g. proximity to a gas giant; inside/outside the stability zone of surface liquid water etc).


The oxidation state of Ti in synthetic and meteoritic hibonite

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Hibonite (CaAl2O4) is a Ti-bearing mineral found in calcium aluminium inclusions (CAIs) and is thought to be the second mineral to condense from a solar composition gas [1]. As such, the crystal chemistry of hibonite could provide insight into the conditions of the early Solar System. Ti may occur as Ti+4 under reducing conditions, with up to 23% of the Ti in meteoritic hibonite previously reported as Ti+3 [2].

We have used X-ray spectromicroscopy (XANES, XPEEM) to determine Ti+3/Ti+4 ratios for a range of meteoritic hibonites, with spatial resolutions between 3 µm and 100 nm. We aim to use this information to investigate if hibonite grains record temporal variations in oxygen fugacity in the early Solar Nebula.

Ti-bearing hibonite samples were prepared at 1400 °C under oxidising and reducing atmospheres using a CO-CO2 gas mixing furnace in order to produce a sample series with 0-100% Ti3+/Ti4+ (where Ti = Ti+4+Ti+3). Neutron diffraction data was used to determine the site occupancy of Ti+4 and Ti+3 in the sample suite. Ti K- and L-edge spectra were recorded for these samples and meteoritic hibonite (c/o A. Bischoff and S. Rout). Spectral features that vary as a function of Ti+3/Ti+4 in the synthetic hibonite series were identified.

The resulting calibration curve was used to determine Ti+3/Ti+4 ratios for the meteoritic hibonite grains. The results show that blue hibonite from CAIs in the unique Acfer094 meteorite and greeny-blue hibonite from a CAI in the El Djouf001 CR meteorite have up to 10% Ti+3/Ti+4. Neutron diffraction data was used to determine the site occupancy of Ti+3 and Ti+4 in the sample suite. Ti K- and L-edge spectra were recorded for these samples and meteoritic hibonite (c/o A. Bischoff and S. Rout). Spectral features that vary as a function of Ti+3/Ti+4 in the synthetic hibonite series were identified.

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Accelerating garnet growth and related dehydration at blueschist-facies conditions, Sifnos, Greece

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While subduction is considered to be a gradual process, consisting of steadily changing pressures and temperatures, metamorphic reactions and mineral growth during subduction may, in some cases, be episodic, or pulsed. Whether the net transformation and accompanying dehydration of subducting material occurs steadily, or in one or more bursts, has important implications for subduction zone petrology and geodynamics.

Here, microdrilling based on major element zoning contours as determined by electron microprobe mapping, from a 4.9-cm diameter garnet in a quartzofeldspathic gneiss from Sifnos, Greece, in the Attic–Cycladic Blueschist Belt, provides information on the rate of mineral growth during metamorphism. Ten concentric growth zones were sampled from the garnet for Sm-Nd geochronology using ID-TIMS. After acid cleansing of mineral inclusions, many of the garnet zones contained very low (0.02 ppm) Nd concentrations, yielding very low sample sizes (~1.5 ng Nd) but very high 147Sm/144Nd (3.4 to 9.8) indicating success in the removal of adverse inclusion effects. These samples were analyzed using a NdO+ with Ta2O5 activator method. Garnet-matrix isochron ages reveal that growth spanned at least 7.3 ± 3.3 Ma from onset in the core at 52.7 ± 3.3 Ma to cessation at the rim just after 45.44 ± 0.21 Ma. Over this timespan, the garnet growth rate accelerated significantly. The innermost 1 cm of garnet (radially) grew at an average rate of ca. 0.9 cm3/Ma, whereas the outermost 0.9 cm grew within just a few 100,000s of years at a growth rate of ca. 100 cm3/Ma. This is an acceleration factor of at least ~2 orders of magnitude.

Rapidly accelerating garnet growth may occur due to gradually changing P and T, or if the PT trajectory crosses closely spaced reaction isopleths. Or, the dehydration of subducted material can provide a synergistic kinetic trigger - a catalyzing fluid - further accelerating garnet growth, and thus water release. Thermodynamic analysis of the garnet forming dehydration reactions and P-T trajectories, can help elucidate the causes and consequences of this acceleration in the net reaction rate.

Microbial mobilization of arsenic from soil of the Mokrsko gold deposit, Czech Republic

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Arsenic mobilization from soil is an issue of concern, as aquatic arsenic can migrate into pristine areas, endangering aquatic organisms and people. Such mobilization in the Mokrsko gold deposit distributes nearly 1.4 kg ha−1 year−1 of arsenic throughout naturally contaminated soil [1]. To gain an understanding of possible biological mechanisms contributing to this transport, mobilization of solid-phase arsenic was investigated in Mokrsko soil microcosms.

Anaerobic microcosms catalyzed rapid release of arsenic from soil containing arsenic-rich goethite, pharmacosiderite and arseniosiderite, mobilizing 33±6% of the total arsenic. Sterilization prevented this transformation. Highly positive correlation between the extracted amounts of arsenic and iron from soil under anaerobic condition implied that microbial reductive dissolution of iron oxides and iron arsenates is responsible for the arsenic release. Sequential extraction analyses designed to determine the arsenic fractionation before and after incubation experiments supported massive dissolution of amorphous and crystalline iron phases in oxalate fractions (65% reduction). The isolation technique enabled the characterization of nine arsenate–resistant bacteria, mostly related to facultative anaerobic genera Bacillus and Pseudomonas, which are used asenrate for respiration [2]. However, the link between arsenic reduction/mobilization and the isolated strains is missing and will be completed soon.

Preliminary observations indicate that a direct microbial arsenic-mobilizing activity exist in the soil, isolated strains are well known arsenic-transforming agents, and thus suggest that dissimilatory arsenic reduction may contribute to arsenic flux from anoxic condition of the Mokrsko gold deposit.


Mineralogical Magazine www.minersoc.org
Geochemical correlations of low-temperature calcite and groundwater in subsurface granite fractures

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Studies of calcite precipitated in bedrock fractures can reveal past groundwater conditions (e.g. [1]). Studies of low-temperature fracture calcite in Proterozoic or Archaean crystalline rocks are, however, very limited, mainly because this calcite usually is very fine-grained or forms rims on older, much more abundant, hydrothermal calcite and is thus difficult to distinguish. Knowledge of chemical characteristics and the correlation with groundwater chemistry is thus scarce for low-temperature calcite in these settings.

In the Proterozoic rock setting at Laxemar, SE Sweden, Quaternary glaciations and related marine transgressions and land uplift, have favoured calcite formation in the bedrock fractures due to repeated introduction and mixing of different waters [2]. We have sampled very fine-grained euhedral low-temperature calcite from these fractures from drill cores (~50 samples, down to 1 km depth) and analysed them for trace elements (using ICP-MS, LA-ICP-MS, WDS) and 87Sr/86Sr, following detailed SEM-studies (e.g. CL) of crystal zonations. Existing groundwater data from the same borehole sections [2] enabled detailed direct calcite-groundwater comparison in terms of both geochemistry and isotopic ratios, e.g. depth-variations. Thereby we tested the utilisation of low-temperature fracture calcite in terms of understanding the groundwater history, also giving input to the understanding of trace element incorporation into calcite in natural systems.

Calcite 87Sr/86Sr-ratios correlated with the groundwater in all sections and ~50% of the sections showed δ18O calcite-groundwater equilibria at ambient temperatures, which suggests potential scattered recent precipitation, e.g. indicated for intruding marine and meteoric water. Calcite isotope signatures also differ considerably from Proterozoic and Paleozoic calcite [3]. The calcite generally showed Me/Ca depth trends consistent with the groundwater for Mn, Mg and Sr. However, only Mn incorporation was in the range expected from experiments [4], which shows the difficulty of applying experimental data onto natural systems, and that 87Sr/86Sr, δ18O, and Mn are the most representative proxies for low-temperature calcite-groundwater interaction.


Recent and fossil chemosynthetic endosymbioses

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Metazoans with chemosynthetic endosymbionts are widespread in marine habitats and respective endosymbioses are known from seven recent animal phyla. However, very little is known about endosymbioses in fossil settings and, hence, ecological significance as well as evolution of endosymbioses in earth history. In the presented project, we investigate the ancient and recent bivalve fauna living at marine sedimentary oxic/anoxic interfaces. Two bivalve species collected from the same benthic environment and a Mediterranean lagoon were studied in detail. The diet of Loripes lacteus is based on thiotrophic gill symbionts. Venerupis aureus is a filter feeding bivalve without symbionts. Analysis of 16S tDNA and fluorescence-in situ hybridisation confirmed the presence of symbionts in Loripes gill tissue. In addition, the presence of one key enzyme of sulfur oxidation (APS-reductase) could be detected by immunofluorescence.

In search of biosignatures associated with thiotrophic chemosymbionts that could also be detected in fossil bivalves, we analysed the isotopic composition of shell lipids (δ13C and δ15N, δ34S). In recent shells and in gill tissue the stable isotopic ratio of carbon is more depleted in the thiotrophic Loripes: e.g., δ13Clipid(18:1FA) -32.2‰, δ13Cconchiolin -25.4‰ than in the filterfeeding Venerupis: δ13Clipid(18:1FA) -28.2‰, δ13Cconchiolin -21.8‰. The isotopic ratios of nitrogen and sulfur are also more depleted in the chemosynthetic Loripes (δ15Nconchiolin +3‰, δ34Sconchiolin -18.5‰) in contrast to filter feeding Venerupis: δ15Nconchiolin +10.1‰, δ34Sconchiolin +13.6‰. Our results give evidence for a major influence of sulfide-oxidizing symbionts on the isotopic composition of organic matter of the host bivalve and are compared with respective data from fossil samples.
Stable isotopes of snow precipitation at Concordia station (East Antarctica)

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The main key factors controlling the oxygen and hydrogen isotope composition of present-day Antarctic precipitation are mainly related to the condensation temperature of the precipitation and the origin of the moisture [1]. In order to calibrate the isotopic tool a multiyear survey from 2006 to 2010 has been carried out in the inland plateau site of Dome C (75°06’S 123°21’E; 3233 m; T=-54.5°C; snow acc. rate 25 kg m⁻² yr⁻¹) in East Antarctica.

Here we present δ¹⁸O, δD and deuterium excess (d) data obtained from daily snow depositions. Observations of deposition amount, shape and size of crystals were also determined. The isotopic data will be also studied as function of synoptic meteorological conditions, using ECMWF re-analyses data and back trajectory models. Preliminary data suggest a good correlation between δD/δ¹⁸O and temperature, both in anti-phase with d at seasonal scale (Fig. 1).

Figure 1: δD, temperature and d data of DC precipitation.


Computational approaches to hydrothermal fluid-rock interaction on nanometer to kilometer scales

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Fluid-rock interaction in hydrothermal systems plays a central role in processes such as the formation of ore deposits, geothermal energy production, and global element cycles. A quantitative understanding of fluid-rock interaction requires looking at vastly different length (nm to km) and time (ps to Ma) scales. Chemical thermodynamics provides the framework that links the scales and computational approaches are essential for both improving thermodynamic models and applying them in the modeling of natural processes.

In spite of decades of research, a universal model of the thermodynamics of fluids at high temperature, pressure and salinity is still lacking, which hampers our ability to quantitatively model fluid-rock interaction in systems such as mid-ocean ridge hydrothermal convection or magmatic-hydrothermal ore formation. Existing equations of state are based on physical concepts that do not reflect the molecular interactions in fluids under those conditions. Hence, molecular simulation has become increasingly popular to better understand the nm-scale physics of hydrothermal fluids. In particular, short-range solute-solvent and solute-solute interactions such as solvation and ion pairing are studied since they are not captured by the most common semi-empirical activity models. While many new insights have been gained from molecular simulation, incorporating them into equations of state is still in its infancy.

On the application side, reactive transport computations combine chemical speciation and fluid transport codes to study the progression of fluid-rock reaction fronts in permeable media on macroscopic scales. These tools have so far only rarely been applied in a hydrothermal context, partly for the reasons outlined above, and partly because most of the available codes are restricted to groundwater flow equations that do not adequately describe the flow of compressible and/or boiling hydrothermal fluids. With the recent revival of research on geothermal systems, new codes are emerging that utilize advanced hydrothermal fluid flow codes that can also simulate flow in complex, “realistic” geometries of fractured geological media. First results indicate that correctly representing geometries is key to understand the causes of heterogeneity in evolving fluid-rock interaction.
A meso-scale laboratory study of stable isotope variations during uranium bioremediation

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We present results from a large-scale column experiment designed to bridge the gap between the field scale and small columns and advance our understanding of the isotopic signatures of biostimulation geochemistry. Stable isotope variations of major elements such as C, Ca and S can identify processes unobservable in concentration data alone but an understanding of these isotope systems must first be developed under controlled biostimulation conditions.

A 1m long, 10cm diameter column was packed with sediment from the saturated zone of the Rifle Integrated Field-Scale Subsurface Research Challenge (IFRC) site in western Colorado. The pore velocity of the column experiment was matched to that of the field, thus providing a direct representation of the first meter down-gradient of the in situ uranium bioremediation injection gallery while ensuring steady flow and boundary conditions. Side-ports along the length of the column provided <20cm sampling resolution, while inert tracers and electron donor were added to the injection solution.

This study has generated an extensive isotopic and biogeochemical reactive transport dataset and provides an unprecedented opportunity to constrain carbon, calcium and sulfur isotopic dynamics. Results include:
1) δ18H and δ16O breakthrough curves yielding a starting porosity of 0.38 decreasing to 0.30 over 42 days.
2) δ13C-labeled acetate allows tracking of carbon originating from electron donor consumption throughout the system.
3) δ44Ca variations in the fluid phase identify two primary controls on Ca: precipitation of carbonates and ion exchange between the fluid and sediment.
4) A δ34S fractionation factor of 12‰ between SO4 and HS- in comparison with a Rayleigh model α of 10‰ indicates variation in α values across the flow path.

These observations are a direct result of the improved spatial and temporal sampling resolution afforded by the experimental design and allow new insight into the highly reactive zone adjacent to contaminant remediation injection wells.

Redox front variability and phosphorus flux across the sediment-water interface

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Phosphorus mobility across the sediment-water interface (SWI) in Missisquoi Bay, a shallow (<15m) bay in Lake Champlain, is largely controlled by redox changes exhibiting diel and seasonal variability that can significantly impact nutrient fluxes and associated cyanobacterial activity. In these iron rich (4-5% w/w total Fe) sediments, reactive P (RP) is strongly correlated to reactive Fe, indicating the mobility of a large portion (30-40%) of the P pool in the sediment is associated with iron oxyhydroxide minerals. We investigated changes in sediments, sediment porewaters, and the overlying water column chemistry and microbiology over three consecutive seasons with detailed monitoring of diel changes at the SWI at each sampling time. Sediment cores were profiled using voltammetric electrodes to characterize porewater redox chemistry (O2, Mn2+, Fe2+, Fe3+, HS-, FeS(aq)). Core profiles show redox conditions become more reducing as the season progresses, with the most strongly reducing conditions present during peak bloom conditions. Redox conditions measured continually over 24-hour periods using in situ voltammetric electrodes positioned at the SWI showed significant changes in redox conditions over diel cycles. Cluster analysis of the data using self-organized mapping techniques indicate redox chemistry across the SWI is a significant controlling component of the system that influences cyanobacterial blooms.

As P fluxes are sensitive to a thin layer of iron oxyhydroxides at the sediment surface, changes in redox chemistry at the SWI significantly impact nutrient flux between the sediment porewaters and the overlying water column. Mesocosm experiments utilizing Missisquoi Bay sediments are underway to characterize phosphorus fluxes between the sediments and water column under different redox conditions at the SWI. Preliminary results indicate that both the direction and intensity of P flux across the SWI are dependent on the redox front position and the frequency of how often the redox front sweeps across the SWI.
Behaviour of Tc(VII) in aqueous solutions in the presence of iron oxides and microorganisms

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This study investigates the redox behaviour of Tc(VII) in a heterogeneous system containing hematite and magnetite with emphasis on transformation of oxidation state through microbial-mediated processes under oxic conditions. Results showed that after a short exposure period under alkaline conditions (pH 8-9) more than 75% of TcO₄⁻ were associated with Fe(II) oxide particles and removed from solution. The removal of Tc from solution may be controlled by reduction of Tc(VII) to Tc(IV) by biogenic Fe(II). Under these circumstances no pronounced effect of the sorption of technetium onto Fe(III) oxide was determined. Sorption of Tc onto hematite is achieved because of presence of specific microorganisms. Results of the combined effect of microorganisms and iron-bearing minerals on Tc (VII) sorption peculiarities have shown that bacteria Arthrobacter globiformis and Cellulomonas cellulans did not have any influence on Tc sorption onto hematite, while micromicete Fusarium oxysporum altered sorption to approximately 85% compared to that in the system without microorganisms. Presence of microorganisms Penicillium sp., Rhodococcus sp and Streptomyces sp. in the tested system induced Tc sorption onto hematite up to 71-82%.

The research has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2011 under grant agreement n° 212287 (RECOsy project) and from Lithuanian Agency for Science, Innovation and Technology (Grant No 31V-6)

Iron oxides of soils from Cenozoic basalts weathering in eastern China: Relationship with climate change

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The Cenozoic basalts are widely distributed from Heilongjiang to Hainan provinces in eastern China, which provide the unique climatic conditions to study basalts weathering. The five soil sequences developed from basalt bedrocks in eastern China were studied, along climate gradient ranging from 200 (Inner Mongolia) to 2,000 mm (Hainan) mean annual precipitation. Magnetic properties, chemical analyses and diffuse reflectance were measured to characterize the iron oxides in soils, since iron oxides are common weathering products and sensitive to response to climate change. Results show that content of free iron oxide, magnetic susceptibility, frequency dependence susceptibility and redness index of surface soil samples are all positively related to MAP, with lowest value in Inner Mongolia samples and highest in Hainan samples. Especially, the content of free iron oxide increases by almost 10 times ranging from 0.5 % to 5.5 % wt. According to similar chemical composition of basalt bedrocks, it can be concluded that climate took most effect on Cenozoic basalt weathering. Further studies are necessary to extract more credible and sensitive indicators like element ratios and mineral index.

This study is funded by the NSF of China (Grant No. 41021002) and China Geological Survey.
Mineral variation induced by CO₂ injection in saline aquifer

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Conceptual modelling

A reactive transport model with TOUGHREACT [1] for the carbon dioxide sequestration into appropriate deep saline aquifer with a depth of 1200m has been involved in this study. Considering storage conditions, a 1D homogeneous conceptual storage formation with a thickness of 50m is constructed, the salt is 1 mol/L, and T is 50°C, carbon dioxide was injected with a speed of 100 kg/s through the central injection well, which lasted for 10a, and the complex geochemical reaction occurs between carbon dioxide and minerals afterward could be known with the model.

![Figure 1: Mineral variation at 1000a after CO₂ injection](image)

Translocation and fractionation of Rare Earth Elements in intensely weathered lateritic profiles in Western Australia

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Three intensely weathered lateritic profiles (GE, MQ I, II) developed on granite with dolerite dykes in Western Australia were studied to investigate the translocation, fractionation and geochemical pathways of rare earth elements (REE) during intense weathering and lateritization. The study has relevance for geochemistry, pedogenesis and environmental chemistry research, and mineral exploration of REE which is one of the most important strategic resources in the world. Geochemical mass balances were calculated based on bulk geochemical compositions. REE-bearing minerals in parent rocks and regolith samples were identified by synchrotron X-ray powder diffraction (SXRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS).

In all three profiles, chondrite normalized REE distributions confirmed that the regolith was developed from granite. High deficiency of REE in the weathered residue indicated strong depletion, except in soils of horizon A in MQ profiles. In MQ profiles, the REE patterns normalized to parent rock represented two layers: accumulation in the upper part of profiles and depletion at the lower part, indicating the regolith below 0.6m depth in MQ I and 1.1m depth in MQ II were weathered in-situ. The source of REE accumulation in surface soil in MQ profiles was unclear, possibly representing biogeochemical recycling. In the GE profile, regolith samples showed great loss of total REE, up to 95 % in the mottled clay (10m deep), followed by ferricrete (83%loss, 3.5m deep).

Depletion of LREE is greater than HREE in all three profiles, except saprolite. In GE profile, a strong linear relationship of (LREE)/(HREE) ratio normalized by parent granite with pH suggested the fractionation of REE in GE profile was controlled by pH. In MQ profile II, main REE-bearing accessory minerals of the parent granite included allanite, fluocerite and epidote. In the weathered regolith, the small grain size of phosphate phases (<20 µm) were surrounded by clay matrix. The geochemical composition and mineralogy of the regolith indicated REE fractionation intensified during advanced weathering.

Using *ab initio* potential to predict thermodynamic properties of fluids and minerals

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Macroscopic thermodynamic properties (PVT properties, phase behavior, chemical potential, speciation reactions, enthalpy etc.) of fluids are determined by intermolecular, and to a less extent, intramolecular interactions, which are functions of molecular distances and angles. Here we present our two studies to demonstrate how to predict the thermodynamic properties through molecular level study.

(1) Using *ab initio* calculated molecular potentials of thousands of different configurations, predicting multi-phase equilibria of methane hydrate, liquid and vapor phases under conditions of different temperature, pressure, salinity and pore sizes. Comparison with the experimental data shows that this model can accurately predict the equilibrium *p*-*T* condition of CH$_4$ hydrate in seawater and porous media with high accuracy.

(2) Based on molecular interaction potential for pure H$_2$O and CO$_2$ and the *ab initio* potential surface across CO$_2$–H$_2$O molecules, we carried out more than one thousand molecular dynamics simulations of the PVTx properties of the mixtures in the TP range from 673.15 to 2573.15 K up to 10.0 GPa. Comparison with extensive experimental PVTx data indicates that the simulated results generally agree with experimental data within 2% in density, equivalent to experimental uncertainty.


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Rock-Eval pyrolysis of the Água de Madeiros Formation (Lower Jurassic) from the Lusitanian Basin, Portugal

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The Lower Jurassic hemipelagic series in the Lusitanian Basin constitutes one of the most important intervals regarding the occurrence of potential hydrocarbon source-rocks in Portugal [1]. One of these units is the Água de Madeiros Formation (Upper Sinemurian to lowermost Pliensbachian), which is composed by organic-rich marl–limestone alternations with several black-shale horizons [2].

Based on the study of this unit in its type locality (S. Pedro de Moel area), about 58 m thick, we present in this work a high-resolution organic geochemical analysis centered in Rock-Eval pyrolysis. Total organic carbon (TOC), determined in more than 170 samples and covering the whole succession, shows a large variation and reaches up to 22 wt.%. A great part of the 78 analyzed samples by pyrolysis present S2 values above 10 mg HC/g rock, reaching a maximum of 78.1 mg HC/g rock. Moreover, these high S2 values are correlative with the highest recorded values of the Hydrogen Index, that shows an average around 400 mg HC/g TOC (maximum of 637 mg HC/g TOC).

Despite these interesting geochemical indicators in terms of good source-rock potential, thermal maturity of the Água de Madeiros Formation in the studied reference section is low (clearly immature), as suggested by *T*$_{max}$ values always below 437 °C.

This work is a contribution to project PTDC/CTE-GIX/098968/2008 (FCT-Portugal, COMPETE/FEDER).

CO₂ degassing and groundwater mixing in the Navajo aquifer, Green River, Utah

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Natural subsurface CO₂ accumulations provide a unique opportunity to understand the long-term fate of anthropogenic CO₂ injected into geological reservoirs. Key parameters include the impact of CO₂ dissolution on reservoir pH and subsequent mineral dissolution / recrystallization processes. Cold-water geysers driven by the degassing of CO₂-saturated fluids in Crystal Geyser, Green River, Utah, allow direct sampling of the underlying CO₂-rich Navajo aquifer. Liquid and gaseous phases have been synchronously sampled during and between geysers eruptions; both water and gas samples have been analyzed for carbon isotopic composition. Water samples have also been analyzed for major and trace elements. The fluid composition changes systematically through the course of an eruption. This reflects mixing of fluid from a deep CO₂-charged aquifer into the shallow Navajo aquifer on the time-scale of eruptions, driven by the pressure perturbation induced by geysering. The evolution of CO₂ degassing has been reconstructed using thermodynamic modelling of the solubility of CO₂ and aqueous phase speciation coupled with a Rayleigh distillation model to reproduce the observed trends in Δ¹³C of gases and dissolved inorganic content of the waters. Results suggest that the Navajo aquifer at depth is undersaturated in CO₂. Degassing is estimated to initiate about 120 meters below the surface, when the fluid rises in the pipe. The pH at depth is calculated to be ~5.35, which is 1.35 pH unit lower than its surface value.

Ce-rich layers in manganese micronodules of the Brasil Basin

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Manganese micronodules (MN) were selected from miopelagic clays of Brasil basin (Atlantic Ocean) to investigate the evolution of their chemical composition depending on the size fraction. We studied bulk MN composition in size fraction: 1000-500, 500-250, 250-100 and 100-50 µm at site 1536 (24°01.1' W, 22°17.6' S, depth 5500 m (depth in core 420-430 cm).

Mn and Fe contents are changed from 23.6 to 31% and from 4.0 to 12.2% respectively. The ratio of Mn/Fe is initially increased from 3.5 to 5.8 and then it is decreased to 2.5 with the increase of MN size fraction.

Changes in iron content resulted in the similar variation in contents of phosphorus, Co, Li, Be, V, Ti, Y, Th, U and rare earth elements. The value of cerium anomaly is decreased from 5.1 to 4 and then it is increased to 14 with the increase of the MN size fraction.

To understand the variations of trace element composition between separate size fractions we analyzed the polished sections of MN by X-ray microanalysis on a scanning electron microscope JEOL JSM-6480LV.

Phase 1 with high manganese and nickel contents and the ratio of Mn/Fe = 9.6 is most widely represented. It is not-layered, enriched in clay material, captured during its formation from the associated sediment. It was formed during early diagenesis and grew at relatively high rate.

Phase 2 is thin-layered, Mn/Fe = 3.2. Phase 1 overlaps unconformably phase 2. It represents the first generation of MN.

Phase 3 is layered, Mn/Fe = 2.1. This generation contains Ce enriched oxyhydroxide phase are contained between their layers.

Enriched in cerium phase 4 is found as the island chains of the substance between the layers of phase 3 and contains an average of about 8% of cerium. It has the lowest Mn/Fe = 1.6 and high Ti and P contents.

Variations in micronodule composition can be explained by influence of two processes – hydrogenous-diagenetic (phases 2-4) and diagenetic (phase 1).
X-ray spectroscopic constraints on complexing of high-field-strength elements in subduction zone aqueous fluids

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Magmatic rocks related to subduction zones commonly display element patterns characterized by depletion of high-field-strength elements (HFSE, i.e., Ti, Zr, Hf, Nb and Ta). The depletion may be due to low solubility in the aqueous fluids that are involved in the processes at subduction zones. The geochemical budget of HFSE is largely controlled by accessory phases such as zircon. Therefore, knowledge is needed on solubility and stability of these phases. Fluid composition should be one of the most important parameters because it can strongly affect complexing of HFSE in aqueous fluids. Complexing with alkalies and silica dissolved in the fluid has been suggested as an efficient mechanism to promote HFSE mobility [1,2]. However, direct evidence on the HFSE speciation in fluids at subduction zone conditions is lacking.

Experimental information on HFSE complexation was obtained for aqueous fluids with HCl, NaOH, Na₂Si₃O₇ (NS3), or Na₂Si₃O₇ + 1 or 5 wt% Al₂O₃, equilibrated with zircon or hafnion in hydrothermal diamond-anvil cells at T up to 750 °C and P up to 1 GPa. On these fluids, XANES and EXAFS spectra were collected in situ at P and T at beamlines ID 24 and ID 26 (ESRF). For NS3 ± Al₂O₃ solutions, measured XANES and EXAFS at the Zr-K and Hf-L₃ edges indicated complexes with 6 oxygens in the first shell. The XANES simulated with FEFF9 [3] based on a Na₂ZrSi₄O₁₁ cluster (as in vlasovite) is in good qualitative agreement with measured spectra. In contrast, 7 oxygens are indicated in the NaOH solution. For HCl solutions, a spectrum simulated for a (Zr,Hf)O₄Cl₃ cluster reproduced qualitatively the features of the experimental spectra. Our results confirm that alkalies and silica dissolved in aqueous fluids may efficiently transport HFSE in the fluids emanating from the subducting slab.

Potential source variation in Munro komatiites: Fred’s and Theo’s Flows, Ontario, Canada

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Munro-type komatiites, also called Al-undepleted komatiites, are volcanic ultramafic rocks characterized by a high MgO content (>18 wt%), and near-chondritic ratios of Al2O3/TiO2 and (Gd/Yb)n.

We present new data of trace element concentrations, measured in two thick, differentiated flows, both Archean (2.7Ga) in age, located in the Munro Township in the Abitibi greenstone belt. Fred’s Flow has komatiitic affinity. It differentiated from a parental magma with about 20% MgO into a series of upper spinifex lavas, a central gabbroic unit and lower olivine-dominated cumulates. Theo’s flow has an Fe-rich tholeiitic affinity. It differentiated from a less-magnesian picritic parental magma into a central gabbro and underlying pyroxene-rich cumulates. The goal of this geochemical study is to better understand the petrogenetic relationship of those two flows.

The results reveal notable differences in REE pattern between the samples. Eight Fred’s Flow units are characterized by moderate to strong depletion in LREE (0.55–(La/Sm)n≤0.99) and relatively flat HREE patterns (0.88–(Gd/Yb)n≤1.20), whereas seven Theo’s Flow units have a convex pattern with (0.83–(La/Sm)n≤1.24) and (1.34–(Gd/Yb)n≤1.63). Elements such as Ba, Cs, Sr and Eu were mobile during metamorphism and/or hydrothermal alteration.

As a whole Theo’s Flow is more enriched in trace elements than Fred’s Flow and its HREE are depleted, indicating that garnet was residual during partial melting. Together with the Fe-rich composition, this may reflect a lower degree of melting and/or a more enriched source, perhaps one with a high eclogite component. Fred’s Flow magmas probably formed by fractional melting of a hotter peridotitic source.

Multiscale melt extraction in the lower crust and upper mantle

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The dynamics associated with melt extraction, including both the movement of melt and the much slower deformation of the solid residue, involves motion on a range of scales. Ultimately melt separation occurs on the crystal scale, while consequent solid deformation occurs on scales of 10s to 100s of kilometers. In order to examine both the solid-state instabilities and melt extraction in detail, we have adopted a multi-scale modeling approach. Crystal scale melt extraction under different amounts of mantle anisotropy is calculated using a lattice Boltzmann method, and a parameterized permeability based on numerous calculations is then incorporated into a multiphase thermal and dynamic model to study the location, timing and flux of melt separating from the crystalline solid. We apply this approach to examine the residence time and extraction rates of melt in lower crustal MASH zones and examine the consequences of foundering of dense crustal roots.

The foundering of dense, mafic residual material from the base of the crust and lithosphere into the underlying mantle has been proposed to explain the long-term chemical evolution of continental crust. Such density instabilities generate solid-state dynamics in the upper mantle surrounding the downwelling material and the return flow of the surrounding mantle. Upwelling regions may generate melting and perturb the flux of magma reaching the base of the crust. We find that large-scale mantle stresses create anisotropy in the permeability structure of the mantle that focuses melt in roughly annular regions surrounding downwelling material. The extent of melting is a function of the degree hydration of the mantle, with the most hydrated conditions resulting in a factor of 3–4 times estimates of background arc melt flux. When the presence of a slab is considered, melt flux is focused preferentially several kilometers toward the backarc region, leaving a magmatic shadow immediately below the downwelling flow.
Sorption and interfacial redox of Sn(II) under anoxic conditions: Magnetite vs. anatase

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The long-lived fission product 126Sn is of substantial interest in the context of nuclear waste deposition in deep underground repositories. However, the redox state (di- or tetravalent) under the expected anoxic conditions is still a matter of debate. We therefore investigated the stability of Sn(II) in the presence of a highly redox-reactive mineral, magnetite (FeIIFeIII2O4), in comparison to a non-redox-reactive, anatase (TiO2).

Sorption experiments were performed at < 2 ppm O2, and redox state and local structure was monitored over time by X-ray absorption spectroscopy (XAS).

We found a rapid (< 30 min) oxidation of Sn(II) to Sn(IV) in the presence of magnetite. Although solubility calculation predicted the precipitation of SnO2, the local structure determined by XAS showed two Sn-Fe distances of about 3.15 and 3.60 Å in line with edge and corner sharing arrangements between octahedrally coordinated Sn(IV) and the magnetite surface, indicative of inner-sphere complexation. The structure of the complex remained largely unchanged up to an equilibration time of 1 month.

After 30 min reaction with anatase, Sn(II) was conserved. However, even with the redox-inert anatase, Sn(II) oxidized to Sn(IV) over time, forming an Sn(IV) inner-sphere complex with Sn-Ti distances at 3.24 and 3.53 Å. Therefore, our results clearly indicate that Sn(IV) is the most relevant oxidation state to be considered even under reducing conditions, and that inner-sphere complexation is a relevant retention mechanism.

Evidence of lime-CO2 evolution and priming effect of agricultural liming

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Agricultural liming contributes significantly to atmospheric CO2 emission from soils [1] and enhances the turnover of soil organic matter (SOC), termed priming effect (PE) [2]. We believe that these impacts of liming acid soils should be factored in our existing soil organic matter (SOM) models but data on magnitude of lime-contributed CO2 and priming effect in a wide range of global acid soils are still few.

Using two acid soils in Japan: (1) an acidic Kuroboku Andisol from Tanashi, Tokyo Prefecture (35°44' N, 139°32' E), and (2) Kunigami Mahji Ultisol of Nakijin, Okinawa Prefecture (26°38' N, 127°58' E), we employed a unique methodology to separate and quantify lime-contributed (13CO2), and SOC-originated (12CO2) CO2-C evolution using Ca13CO3 (13C 99%) as lime and tracer.

Our experimental data have confirmed that (1) lime contributes heavily to CO2 evolution, and (2) liming acid soils increases SOC turnover. On the average, lime-CO2 was 76.84% (Kuroboku Andisol) and 66.36% (Kunigami Mahji Ultisol) of overall CO2 emission after 36 days, indicating that the mineralization of lime-carbonates is the major source of CO2 emission from acid soils during agricultural liming. The calculated PE of lime (Kuroboku Andisol, 51.97-114.95%; Kunigami Mahji Ultisol, 10.13-35.61%) was entirely 12C turnover of stable SOC since the soil microbial biomass (SMBC), a labile SOC pool, was suppressed by liming in our experiment.

Liming can influence the magnitude of CO2 evolution from agricultural ecosystems considering global extent of acid soils and current volume of lime utilization. The measured PE of liming in SOC is large and can significantly alter atmospheric CO2 evolution from agricultural ecosystems.

Co-evolution of clay-sized organic and mineral constituents during initial soil formation

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Clay fractions from a soil chronosequence (Switzerland) after retreat of the Damma glacier (15, 75 and 120 yrs) and from mature soils outside the proglacial area (> 700 yrs) were used to elucidate the evolution of organo-mineral associations during initial soil formation.

The chemistry of clay-bound organic matter was assessed by 13C NMR spectroscopy and the contents of amino acids and neutral sugar monomers were determined by acid hydrolysis. The mineral phase was characterized by X-ray diffraction, oxalate extraction, N2 adsorption, and cation exchange capacity at pH 7 (CECpH7), before and after H2O2 treatment.

The OC loading of the clay fractions strongly increased within about 100 yrs of soil formation. This resulted in decreasing specific surface area (SSA) of the mineral phase and increasing CECpH7 which is in line with XRD analysis as no significant transformations of clay minerals were detected.

The SSA of H2O2-treated clay fractions were strongly related to oxalate soluble Fe (FeOx) and a strong correlation was found between increasing contents of FeOx and OC with soil age.

Clay-bound OC of the 15-year-old soils was of refractory nature owing to high proportions of carboxyl C and aromatic C which may be ascribed to inherited OC. With increasing age (75 and 120 yrs), the relative proportions of carboxyl and aromatic C decreased. This was mainly associated with increasing O-alkyl C proportions, whereas accumulation of alkyl C is detected only in the mature soils. These findings are in line with the amounts of carbohydrates which predominately derived from microbial input. Proteins accumulated to a similar extent as carbohydrates and H2O2 resistant OM showed very low C/N ratios.

The formation of organo-mineral associations starts with the sorption of microbial-derived proteinaceous compounds and carbohydrates on mineral surfaces which are mainly provided by ferrihydrite. The sequential accumulation of different organic compounds and the large OC loadings point to layering of OM during the evolution of clay fractions.

Composition of error in LA-ICP-MS U/Pb geochronology: Lessons from the processing of standard measurement series performed in ten laboratories

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We have studied the error propagation and the composition of the error of the calculated U/Pb ages of standards measured in ten laboratories by laser ICP-MS technique. These laboratories used different mass spectrometers, laser cells and instrumental settings. The data reduction was performed by several alternative methods e.g. using Arithmetic Mean of Ratios (AMoR), Ratio of Means (RoMa), Median and regression methods and the residual errors of these procedures were compared. The effect of outlier rejection using the standard 2-sigma method and an iterative outlier-testing method was also studied.

Beyond the classical measures of the precision of the age like concordance we performed several experiments to express the scatter of the data obtained by the the laser ablation.

The so called Extra Poissonal Error is recommended for the optimization of the dwell times of the analytes.

The ratio of the mean and the Tzero intercept (of regression) gives a more robust measure for the fractionation than the ratio of the means of first half / second half of the ablation signal.

The influence of the drift through a measurement session was also studied.

The calculations were performed by the UranOS software: www.sediment.uni-goettingen.de/staff/dunkl/software/
Rapid expansions in biological metal utilization

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The fundamental chemistry of trace elements dictates the molecular speciation and reactivity both within cells and the environment at large. Using protein structure and comparative genomics, we elucidate several major influences this chemistry has had upon biology. All of life exhibits the same proteome size-dependent scaling for the number of metal-binding proteins within a proteome. This fundamental evolutionary constant shows that the selection of one element occurs at the exclusion of another, with the eschewal of Fe for Zn and Ca being a defining feature of eukaryotic proteomes. Remarkably, most of known metalloenzymes evolved during two transitional eras. First, development of protein structures for metal homeostasis coincided with the emergence of metal-using proteins, which predominantly bound metals abundant in the Archean ocean. Potentially, this promoted the diversification of emerging lineages of Archaea and Bacteria through the establishment of biogeochemical cycles. In a later expansion, over 75% of known Zn binding structures evolve at the same time as the Eukaryotic superkingdom emerged. These Zn-binding proteins are fundamental to eukaryotic cellular biology, while the localization to the nucleus indicates that they are diagnostic features of this superkingdom. Zn bioavailability may have been a limiting factor in eukaryotic evolution. In both scenarios, the newly evolved metalloenzymes would drastically change cell biology and by extension, geochemistry.

The role of extracellular organic matter (EOM) in the nucleation and growth of microbial carbonates

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Microbes are key players in the global carbon cycle, where they influence the balance between the organic and inorganic carbon. Microbial populations can be organized in microbial mats, which can be defined as organosedimentary biofilms that exhibit tight coupling of element cycles. Complex interactions between mat microbes and their surrounding environment can result in the precipitation of carbonate minerals (i.e., microbialite). This process refers as ‘organomineralization sensu lato’, which differs from ‘biomineralization’ (e.g., in shells and bones) by lacking genetic control on the mineral product. Organomineralization can be: (1) active, when microbial metabolic reactions are responsible for the precipitation (“biologically-induced” mineralization) or (2) passive, when mineralization within a microbial organic matrix is environmentally driven (e.g., through degassing or desiccation) (“biologically-influenced” mineralization). Two tightly coupled components that control carbonate organomineralization s.l.: (1) the alkalinity engine and 2) the extracellular organic matter (EOM), which is ultimately the location of mineral nucleation.

The EOM is composed of two main carbon pools: the high molecular weight extracellular polymeric substances (EPS) and the low molecular weight organic carbon compounds (LMW-OC). Both pools play a critical role in carbonate precipitation by providing Ca$^{2+}$ and CO$_3^{2-}$ as well as a nucleation template for mineral growth. EOM contains several negatively charged functional groups, which, depending on the pH, can be deprotonated (each group has unique pK value(s)) and, thus, bind cations. This binding capacity can deplete the surrounding environment of cations (e.g., Ca$^{2+}$, Mg$^{2+}$) and, thus, inhibits carbonate precipitation. Therefore, organomineralization is only possible if the inhibition potential is reduced through (1) oversaturation of the EOM binding capacity or (2) EOM degradation.

Studying microbe-mineral interactions, particularly the role of EOM in carbonate formation, is essential in the investigation of early life (e.g., definition of biosignature), especially at the interface between the biotic and prebiotic worlds, where newly formed organic matter could have strongly influenced the nucleation and growth of minerals, notably carbonate.
Advances in the understanding of atmospheric impacts of volcanic ash emissions since Eyjafjallajökull 2010

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Volcanic emissions contain a mixture of gases, and aerosol and silicate ash particles [1]. Volcanic aerosol injected high into the stratosphere may impact atmospheric chemical cycles, or interact with solar and terrestrial radiation and influence climate. Airborne ash and sulphate aerosol in the troposphere, in contrast, has shorter-lived atmospheric and climatic impact. The eruption of Eyjafjallajökull in April and May 2010 brought the atmospheric impacts of volcanic ash emissions to global attention through prolonged grounding of commercial aircraft and subsequent impact on the global economy. In response, the research community engaged across disciplines at an unprecedented scale to provide information, often in real-time, on eruption source parameters, airborne ash characteristics and fallout. One year on from the eruption, we investigate what new knowledge on the impacts of volcanic ash emissions has emerged.

Measurements of ash in the Eyjafjallajökull volcanic cloud from surface [2] and aircraft-mounted instruments [3], and satellite-based sensors combined with modelling [4] tracked the evolution of the ash emissions and provided sometimes contrasting indications of spatial variation in airborne ash concentration. Satellite measurements suggest highly heterogeneous structures with pockets of highly concentrated ash; in contrast the ground-based lidar network suggest low concentrations and highly dispersed ash layers, while airborne measurements suggest concentrations no greater than 1 mg m⁻³ in thin layers [3]. Ash aggregation, while not generally included in ash transport and dispersion models, played an important role in the sedimentation of fine ash generated by the eruption [5]. Finally, it is clear, post-analysis, that there is a need for assiduousness when applying standard atmospheric measurement techniques to the study of volcanic ash clouds.


The geochemical characteristics of beach sediments of the Finike Gulf (Southwest Turkey)

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In the Finike Gulf (SW-Turkey), geochemical characteristics of modern beach sediments were studied to determine their possible economical potential with respect to marine placer deposits and related depositional, transportation and provenance factors. This study was supported by the the Scientific Research Projects Office of the Ankara University. The study comprised geomorphological field observations, sediment sampling and laboratory analysis (i.e., grain size, multielement composition, total heavy minerals). Within this context, in September 2009, large number of modern-surface sediment samples were collected from the foreshore and backshore sub-environments of the beaches of the Finike Gulf. Sand with varying proportions is the dominant grain size in beach sediments. Element composition of sediment samples was mostly comparable with that of average earth’s crustal rocks. However, relatively higher concentrations were measured for Ni (up to 451 ppm) and Cr (2548 ppm). These values can be related to the presence and wide occurrences of ophiolitic rocks (known as “Antalya Nappes”) on the coastal hinterland [1]. The study is still going on.

Facies and petrochemical characteristics of the Tertiary aged Tekkeköy (Samsun) area volcanics, NE Turkey

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Tertiary volcanics crop out widely in the eastern Pontide, NE Turkey. Of these, the Tekkeköy (Samsun) area volcanics in a E-W trending shallow marine basin lie along the Black Sea coast in the western part of the Eastern Pontide Tertiary Volcanic Province (EPTVP) [1]. The volcanic facieses are dominantly basaltic pyroclastics, less basaltic lava flows, dykes and trachytic dome. The basaltic rocks contain plagioclase, augite and rare olivine with porphyritic, microlitic porphyritic, intergranular and locally cumulophyric textures. Trachytic rocks are composed of plagioclase, sanidine, hornblende and biotite with trachytic texture.

Petrochemically, the volcanics can be classified as basalt, trachybasalt, basaltic-andesite, basaltic trachyandesite and trachyte, and exhibit mildly alkaline to subalkaline with medium- to high-K in character. Major oxides and trace elements versus SiO₂ variations show negative correlation for Al₂O₃, Fe₂O₃*, CaO, TiO₂, P₂O₅, MnO, MgO, Co and V whereas positive correlation for K₂O, Na₂O, Rb, Ba and Zr, most of which can be explained by fractionation of cpx+Fe-Ti oxide in mafic rocks, and hornblende +apatite+Fe-Ti oxide in felsic rocks. Besides increase in U and Th with increasing oxide in mafic rocks, and hornblende +apatite+Fe- Ti oxide in most of which can be explained by fractionation of cpx+Fe-Ti oxide in mafic rocks, and hornblende +apatite+Fe-Ti oxide in felsic rocks. Besides increase in U and Th with increasing SiO₂ from mafic to felsic rocks may be regarded to small amount of crustal assimilation. N–MORB normalized trace elements patterns show enrichment of LILE (Sr, K, Rb, Ba) and depletion in HFSE (Th, Ce, Zr, Ti, Y) with negative Ta and Nb anomaly, suggesting a subduction and/or crustal contamination signature. The chondrite–normalized REE patterns of mafic to felsic samples are similar to each other revealing a common parental source magma (s) for the volcanics. The REE patterns have also concave in shape with marked light REE enrichment and heavy REE depletion, implying effect of significant cpx and hornblende controlled fractionation during the evolution of the volcanics. Facies and petrochemical features of the Tekkeköy volcanics suggest that they may evolved from parental magma (s) derived from an enriched lithospheric mantle source, and correlate others of collisional-post collisional volcanics in the EPTVP.

The evolving landscape of U-series sea level chronologies

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Several factors have contributed to the recent movement within the U-series dating community to promote more consistent practices that will ultimately produce more robust chronologies both within and between individual laboratories. First, instrumental and methodological advances have greatly increased the precision of the U-series technique. One consequence of this improved analytical capability is the amplification of the impact of interlaboratory differences in standardization techniques. Second, publication of revised decay constants for $^{230}$Th and $^{234}$U as well as inconsistent adoption of these constants across the community have led to issues in the appropriate comparison to and conversion of legacy data. This becomes a problem when new data are contextualized with regional or global datasets generated with different decay constants, and requires the availability of raw data and standardization procedures that have not always been routinely published. Third, there has been an increasing demand for more precise constraints on both the absolute and relative timing of past sea level changes to provide empirical constraints on future sea level behavior. This pressure comes from both within and beyond the scientific community, and routinely encourages scientists to push their interpretations to the very limits prescribed by the data.

All of these issues play into the ongoing debate about the appropriate identification, interpretation, and handling of data from corals that have been compromised by open-system behavior. It is increasingly apparent that modeled open-system ages versus screened closed-system ages lead to notable discrepancies in chronologies of past sea level change. This debate is compounded by the recognition that uranium isotope ($^{234}$U/$^{238}$U) ratios of seawater may have varied significantly over the last glacial cycle. Understanding this variability, and its cause, are critical to both the modeled open-system and closed-system approaches to building chronologies of sea level change.

These considerations will be addressed in the context of amalgamating and integrating disparate datasets of sea level change during the last interglacial. This analysis provides impetus to establish more consistency in the analysis, reporting, and treatment of U-series data that will pave the way to advancing our understanding of ice sheet dynamics.

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Multiscale modeling of ionic transport in charged clays

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Modeling the solute transport through a pore network in clays is a crucial issue in better understanding its macroscopic transfer processes. Indeed, although the microscopic (sub-nanometer scale) and macroscopic (multi-microns scale) transport properties in such materials are now well known, a lack remains between these two scales.

This study aims at developing a model representing as accurately as possible the main macroscopic properties of a clay sample. In our model, the material is represented by a pore network in which each pore is connected to an other by a channel.

Figure 1: Zoom on an unit cell of the Pore Network Model lattice.

A Lattice-Electrokinetics scheme [1,2] is used to model the microscopic transport properties through the interporal channels (nm scale). Then macroscopic properties (µm scale) are calculated from the microscopic ones using a Pore Network Model (PNM) [3]. Indeed, the calculation of the macroscopic transport properties through a pore and channel network using PNM requires a good understanding of the microscopic ion transport processes (at the channel scale), that depend on the pore and channel properties. Thus, the key question we address here is “How do the transport properties depend on these pore and channel properties?”

The effect of sodium fluoride on soil microbial activity during organic matter decomposition – A calorimetric approach

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Results and Discussion
Soils exposed to intensive emissions from phosphoric fertilizers and aluminum industries or other fluoride sources have high fluoride concentrations [1]. Fluorides found in soil can affect its microbial activity which can be measured using calorimetric methods [2]. Soil samples were collected at the Agricultural Station of the University. During successive experiments, at 0; 0.05; 0.1; 0.25 and 0.55 % fluoride content and 1 mg glucose in 1g of soil changes in microbial activity were investigated by the calorimetric method. Soil moisture corresponded to 60 % of the maximum water-holding capacity. The changes in the rate of heat production, peak time, total heat effects and the apparent rate constant parameters were used to characterize the glucose biodegradation processes in soil. Sodium fluoride introduced into the soil in the amount corresponding to 0.25 and 0.55 % of fluoride ions decreased the rate of glucose biodegradation. The total heat effects of the studied processes were higher in the presence of fluorides in comparison with soil samples containing no sodium fluoride. The obtained results suggest that despite the reduced rate of glucose biodegradation in the presence of higher doses of sodium fluoride, this compound contributes to an increase in the bioavailability of soil organic substrate for microbial decomposition,