Compacted Nanoparticles for Quantification in LA-ICPMS

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Gray et al. did first studies of LA-ICPMS in 1985 [1]. Ever since, extensive research has been performed to overcome the problem of so-called “non-stoichiometric sampling” and/or analysis, the origins of which are commonly referred to as elemental fractionation (EF). EF mainly consists of laser-, transport- and ICP-induced effects, and often results in inaccurate analyses as pointed out in, e.g. references [2,3].

A major problem that has to be addressed is the lack of reference materials. Though the glass series of NIST SRM 61x have been the most commonly reference material used in LA-ICPMS, heterogeneities have been reported for some sample charges [4,5]. In addition, geological relevant elements such as Ti, Fe and Mg are present in very low concentrations only and thus not well suited for calibration. Elements such as Rh, Ru, Pd, Pt and Au (PGEs) are either absent or present in very low concentrations.

The production procedure of glass limits the implementation of these elements into the glass matrix at concentrations required for many applications. Therefore, alternative methods for the production of calibrants were studied concerning the implementation of PGEs into Silicates, Carbonates, and Iron-Sulfides, which are homogeneous at the spatial resolution commonly used in microbeam techniques.

Flame synthesis was used to reproduce the NIST 610 matrix at similar concentrations. Furthermore, PGEs and other elements were added to the matrix. The resulting powder consists of nanoparticles in the size range of 20-50 nm, which is well below the commonly crater diameters used in LA-ICPMS. The PGE concentration is for most of the elements around 500 μg/kg. Multiple analyses of these powders provide a RSD for PGEs in the order of 1-3 %.

The difference between the pressed powder analysis and calcinated pellets shows indistinguishable results for most of the elements. The setup of production, preliminary results and first figures of merit will be discussed.


Evaporation behavior of forsterite (Mg2SiO4) in a H2O-H2 gas

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Forsterite (Mg2SiO4) is one of the most abundant crystalline silicates in extraterrestrial materials and in circumstellar environments, and its evaporation behavior has been intensively studied in vacuum and in the presence of low-pressure hydrogen gas [e.g., 1-4]. It has been known that the evaporation rate of forsterite is controlled by a thermodynamic driving force (i.e., equilibrium vapor pressure), and the evaporation rate increases linearly with pH2 [5] in the presence of hydrogen gas due to the increase of the equilibrium vapor pressure. The deviation of the actual evaporation rate from the ideal evaporation rate, which is given by an equilibrium vapor pressure and the kinetic theory of gases, is expressed as an evaporation coefficient (=Actual rate/Ideal rate) ranging from 0 to 1 (a measure of kinetic hindrance for evaporation). The evaporation coefficient is 0.1-0.01 for evaporation of forsterite in vacuum and in hydrogen gas depending on temperature and crystallographic orientation of the evaporating surface [e.g., 1-4]. Besides the free-evaporation dominated regime [FED] (evaporation in vacuum) and the hydrogen-reaction dominated regime [HRD] (evaporation in hydrogen gas), Tsuchiyama et al. [5] proposed another evaporation regime called H2O/H2 buffer-dominated regime [HBD] as a dominant evaporation regime for forsterite in protoplanetary disks at temperatures of <1400 K and under H2O-rich conditions. In the HBD regime, the equilibrium vapor pressure of forsterite is not controlled by pH2 [5], but by the H2O/H2 ratio in the ambient gas. In spite of its potential importance, no experimental study has been done to investigate the evaporation kinetics in the HBD regime. We have performed evaporation experiments on forsterite at low pressures with controlled H2O/H2 ratios, and have found that the evaporation rates are controlled by the H2O/H2 ratio as proposed by [5] and that the evaporation coefficient is consistent with that in FED and HRD regimes.


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Southern Hemisphere orbital forcing and its effects on CO₂ and tropical Pacific climate

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The western Pacific warm pool (WPWP) is an important heat source for the atmospheric circulation and influences climate conditions worldwide. Understanding its sensitivity to past radiative perturbations may help better contextualize the magnitudes and patterns of current and projected tropical climate change. Here we present a new Mg/Ca-based sea surface temperature (SST) reconstruction over the past 400 kyr from the Bismarck Sea, off Papua New Guinea, along with results from a transient earth system model simulation. Our results document the primary influence of CO₂ forcing on glacial/interglacial WPWP SSTs and secondary effects due to changes in wind-driven tropical boundary currents. In addition to the SST, deep ocean temperature reconstructions from this core are linked with Southern Ocean temperature and sea-ice variations on timescales of ~23 kyr. It is proposed that Southern Hemisphere insolation changes serve as pacemaker for sea-ice variations in the Southern Ocean, which in turn modulate windstress curl-driven upwelling of carbon-rich waters, hence controlling atmospheric CO₂ and tropical WPWP temperatures.

CO₃, OH, and halogen microanalysis in apatite group minerals

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The last three years have seen a re-evaluation of microanalytical methods for apatite, including standards. This presentation presents new data and reviews recent results for analytical methodology for C, OH, and halogens for apatite minerals.

Initial documentation of anisotropic beam-driven halogen diffusion [1] in apatites, long ignored, has been confirmed and shown to be more complex for varying F and Cl concentrations [2]. Quantitative analysis requires constraints on crystal orientation for both unknowns and standards, as well as controlled history under the electron beam. Analytical methods presented here use accelerating voltages <10keV and short analytical durations to clearly define the rise and fall in count rates for zero-time regression. Data in hand show that F and Cl are rapidly lost from the apatite during analysis at 15 and 20 keV in all crystal orientations. Analyses are unlikely to be valid without regression-to-zero techniques for unknown and standard. Uncertainties in electron microprobe halogen analyses are magnified in OH calculated by the difference method.

Problems with FTIR analysis of apatite (strongly polarized OH stretching, crystal size, sample thickness) have been overcome to allow analysis of unpolished mineral separates and experimental products. Polarized radiation is preferred for OH analysis, but unpolarized radiation can be used on (100) sections [3] and euhedral synthetic crystals. The A and B type carbonate substitutions are not strongly polarized, allowing use of unpolarized radiation.

Carbonate and OH standards for apatite are lacking. A large FTIR dataset for naturally occurring apatites shows homogeneities or complexities precluding their use as standards. For example, Durango fluorapatite shows trimodal OH distribution (n=5570). Synthetic standards are under development.

Previously published apatite studies should be carefully evaluated in the light of these results.

Thermochronological investigation of seismogenic fault zones: an overview and examples from Japanese Islands

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The timing of faulting episodes can be constrained by radiometric dating of fault-zone rocks. Fault-zone material suitable for dating is produced by tectonic processes, such as (1) fragmentation of host rocks, followed by grain-size reduction and recrystallization to form mica and clay minerals, (2) secondary heating/melting of host rocks by frictional fault motions, and (3) mineral vein formation as a result of fluid advection associated with the fault motions. The thermal regime of fault zones consists primarily of the following three factors: (a) regional geothermal structure across the fault zone and background thermal history of studied province bounded by fault systems, (b) frictional heating of wall rocks by fault motions, and (c) heating of host rocks by hot fluid advection in and around the fault zone. Thermochronological methods widely applied in fault zones are K-Ar ($^{40}$Ar/$^{39}$Ar), fission-track, and U-Th methods. The thermal sensitivities of individual thermochronological systems are briefly reviewed, which critically control the response of each method against the thermal processes. Based on the knowledge above, representative examples as well as key issues are highlighted to date fault gouges, pseudotachylytes, mylonites and carbonate veins, placing valuable constraints upon geological, geomorphological and seismological frames. Finally, the results from Japanese Islands are presented, including the Shimanto belt, as examples for multiple applications of thermochronological methods.

Geobotany and biogeochemistry of Sungun Copper deposit, northern Iran: An implication to mineral exploration

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Sungun porphyry copper deposit is located in the east of Azarbaidjan, NW of Iran. Geobotany is one of the important methods in mineral exploration. In this method the plants represented paid a heavy metal track. Geochemical prospecting has been carried out on distribution of Zn, Pb, Cu, As, Cd and Mo in the plant species and soil of the Sungun Cu-Mo deposit. Field prospecting has been indicated that Anthemis nobilis, Crepis sancta and Picnonomonacarna are the main plant species in the area. Geochemical results indicated enrichment of Mo, As and Cu (Cu > Mo > As) which is correlated with concentration of the metals in associated soil. Anthemis nobilis has been shown the greatest capability for accumulating Cu and Mo in its tissues through soil so it could be used as a bioindicator for mineral exploration. This plant with other plant species such as Crepis Sancta and Picnonomonacarna have high scavenging ability for Mo and Cu from the soil and could cause serious environmental and health problems in the living organisms of the area.
Density control on formation of crustal magma storage system

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Magma reservoirs probably grow by repeated sill-like intrusions. We investigate the conditions for repeated crustal intrusions at the same depth by a feeder dike before a permanent molten reservoir can form. Sill formation requires that magma within a dike develops an overpressure large enough to overcome the strength of surrounding rocks. An efficient mechanism to achieve this involves ascent through layers with decreasing density, such that magma becomes negatively buoyant above some structural interface. To significantly affect dike ascent, the density change in country rock must occur over a thickness of the order of the length-scale for the inflated nose region that develops below the dike tip. This characteristic length depends on the elastic properties of the host rocks, on magma buoyancy and on the flux of magma. It is usually around 1 km for basaltic magmas, comparable to the typical thickness of sedimentary strata and volcanic deposits. The overpressure that develops at the density inversion level is determined by the vertical extent of the inflated dike nose region above that level, and hence is related to the volume of magma in that region. Thus, sill formation also requires that the total volume of magma available in an individual intrusion event exceeds a threshold value.

Pressure variations in metamorphic rocks: Implications for the interpretation of petrographic observations

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During mineral reaction, the overall mechanical state of a rock is very important. Rock strength may control the reaction progress from 0 to 100% which may result in the development of stress, and therefore pressure, variation on all scales. Hence, considering the interplay of metamorphic reaction and mechanical properties is critical for correctly interpreting microstructural observations in metamorphic rocks and correct quantification of the processes.

Stresses that develop during deformation of geologic materials can be responsible for the formation and preservation of GPa-level pressure variations. Considering that the typical value of the lithostatic pressure at the base of the continental crust is ~1 GPa, GPa-level variations make the interpretation of depth from pressure problematic for crustal metamorphic rocks. Such pressure perturbations are more apparent on a small scale (nm to mm), where, in some cases, they can be directly measured by spectroscopic methods. However, the non lithostatic pressure variations can also be relevant to larger (crustal) scales. Schmalholz and Podladchikov [1] have recently shown that even when rocks are deformed in a “weak” crustal- scale shear zone, force balance across the shear zone requires that pressure will not be smoothly varying with depth but it will be paradoxically higher within the shear zone.

The recent microstructural observations and mechanical models question our current quantification approach in metamorphic petrology based on the lithostatic assumption. The recent data have therefore opened horizons for new approaches and new physically rigorous and geologically realistic interpretations of our petrographic observations. Such approaches would contribute to our better understanding the processes in the Earth interior.

Structural simulation on silica crystals and glasses

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Molecular dynamics simulation has been used to investigate the similarity and dissimilarity in dynamical structural changes between silica crystals and glasses. Many simulation studies have been performed for quartz, cristobalite and silica glasses [1-3], however, there is scarcely any simulation studies on tridymite. The structural building block is the same between in tridymite and cristobalite, nevertheless, structural changes due to the thermal effects is more complex in tridymite than in cristobalite. Such complexity hinders the theoretical study. First, the structural chages of tridymite phase due to thermal effects are investigated by using molecular dynamics simulation. Next, the calculated complex structural changes are compared with those of the other structures such as cristobalite and glasses. Firnally, we discuss the similarities and dissimilarities in dynamical structural changes in terms of microscopic structure.


Ontogenetic stable isotope records of modern planktic foraminifers from Sagami Bay, Japan

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Stable oxygen ($\delta^{18}$O) and carbon ($\delta^{13}$C) isotopes recorded in planktic foraminiferal tests are widely used as proxies for paleoceanography and species ecology. Of such isotopic investigations, ontogenetic isotopic profiles are thought to record foraminiferal ecological information such as depth habitat or symbiotic relationship. Though size-related isotopic series, achieved by analyses of a series of shieved fractions, seem to reflect ontogenetic profiles of species, isotopic profiles through “individual ontogeny” have rarely been examined. In this study, we report ontogenetic isotopic information of individual specimens, together with in situ water column oceanographic information ($\delta^{18}$O$_{sw}$, $\delta^{13}$C$_{DIC}$, temperature, salinity, nutrient, and chlorophyll-a).

We examined ontogenetic stable isotopic profiles of planktic foraminifers by performing chamber-by-chamber analyses within a single individual. Each chamber is dissected from an individual and analyzed by specially designed continuous-flow mass spectrometry system [1]. Instead of size-related analyses, this method enables us to reveal individual ontogenetic information free from mixing of seasonal variability. Four modern species, obtained by vertical towing at Sagami Bay, Japan, were analyzed: Globigerinoides sacculifer, Globigerinoides conglobatus, Neogloboquadrina dutertrei, and Globorotalia inflata.

The ontogenetic $\delta^{18}$O profiles showed overall increase for all species, suggesting the ontogenetic deeper migration commonly found in modern species. While $\delta^{13}$C showed steep increase especially in a juvenile stage for all species, the increase continued to the last chambers only in symbiont-bearing globigerinoidid species. $\delta^{13}$C of asymbiotic species becomes decrease after the rapid increase in the juvenile stage. Comparing these records to water column chemical and physical data, regardless of their adult habitat depths, all foraminifers analyzed start their calcification, hence their ontogeny, near the thermocline, which corresponds to chlorophyll maxima and nutrient-depleted depth.


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Magma feeding system of Fuji volcano, Japan

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Fuji volcano is known for its perfect cone shape and it is the largest among Japanese Quaternary volcanoes. In the last 100 kya, Fuji has erupted only basalt magma (≫99 vol%), but its eruption style changed (from debris flow and tephra dominant Ko-Fuji or Older Fuji, to lava flow dominant Shin-Fuji or Younger Fuji) at ~15 kya BP. Origin of the voluminous yet monotonous basalt production in Fuji volcano have been discussed but remain unanswered. Here we report the first high-pressure melting experimental results on Fuji basalt (Hoei-IV, AD1707) and demonstrate that its main magma chamber is located at ca.25 km depth. We show seismic tomographic images of Fuji volcano for the first time, which reveals the existence of strong upwelling flow in the mantle and its connection to the voluminous lower crustal magma chamber (see Fig.1).

Very frequent low frequency earthquakes just above the magma chamber (open circles in Fig.1) may be due to the injection of basalt magma and/or fluids. The total lack of silica-rich rocks (basaltic andesite and andesite) in Fuji volcano must be due to the special location of the volcano. The plate boundary between the Eurasia plate and the subducting Philippine sea plate is located just beneath Fuji volcano (~5 km depth). Large tectonic stress and deformation associated with the plate boundary inhibit the survival of a shallow level magma chamber, which would allow the evolution of basalt to silica-rich magma (as observed in all other volcanoes in Japan, e.g., Hakone, Izu Oshima).

Migration of radiocesium and radioiodine in soil-water-river system related to Fukushima-Diichi Nuclear Power Plant Accident

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Radionuclides such as radiocesium and radioiodine were emitted from the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident caused by the Great East Japan Earthquake and Tsunami on March 11, 2011. Highly contaminated areas spread in the northwest direction from FDNPP in Fukushima Prefecture, which mainly resulted from the distribution of the wet deposition on March 15 [1]. After the deposition, vertical profiles of the radionuclides in soil in Fukushima showed that radioesium and radiiodine have been retained within 5 cm from the surface. Analysis of particulate matters and sediment particles in rivers in the region showed that radioesium is enriched in finer fractions.

These results suggested that radioesium and radioiodine have high affinity to soil particles. For radioesium, adsorption on clay minerals have been indicated. Thus, extended X-ray absorption fine structure (EXAFS) spectroscopy has been used (i) to characterize structure of surface complex of cesium with 2:1 phyllosilicate and (ii) to understand the reduction of the adsorption in the presence of humic substances. We also found a correlation between (i) the fraction of inner-sphere complex among total cesium species adsorbed on the soil particles and (ii) Radiocesium Interception Potential (RIP) value, which suggests that RIP is dependent on the mineral content and humic substances.

About 30% of radioiodine leached by NaOH solution (pH 10.5) from the soil collected one month after the accident [2]. When the NaOH solution was acidified to pH 2, more than 60% of radioiodine in the solution precipitated possibly with humic materials that can bind iodine in the polyorganic structure. This leaching-precipitation behavior suggests that a part of iodine is in the organic form in the soil, which can be a reason for the low leaching rate in the soil by water. The formation of organic iodine in natural soil has been suggested also by XAFS using X-ray microbeam [3]. The formation of organo iodine species proceeds in a relatively short period, such as within a week or a month. Thus, the formation of organo iodine is possible for radioiodine in the soil.


Fig. 1 Seismic tomography beneath Fuji volcano. EW section

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Seasonal change of Iron species and concentration of soluble Iron in the atmosphere in Northwest Pacific region based on the analysis of aerosols collected in Tsukuba, Japan

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Atmospheric iron (Fe) can be a significant source of nutrient for phytoplankton in remote ocean, which in turn has a large influence on Earth’s climate. Whether Fe in aerosol can be bioavailable or not depends mainly on the soluble fraction of Fe. However, factors controlling the soluble fraction of Fe have not been understood fully, since there can be many factors controlling the fraction. In this study, Fe species, chemical composition, and soluble Fe concentration in aerosol collected at Tsukuba through a year were investigated to identify the factors controlling the amount of soluble Fe supplied into ocean. The concentration of soluble Fe in aerosol is correlated with those of sulfate and oxalate which originate from anthropogenic sources, suggesting that soluble Fe is mainly derived from anthropogenic sources. Moreover, the concentration of soluble Fe (%) is also correlated with enrichment factors (EF) of vanadium (V) and nickel (Ni) emitted by fossil fuel combustion. These results suggested that the degree of Fe dissolution is controlled by the magnitude of anthropogenic activity such as fossil fuel combustion. In addition, XAFS was performed in this study to identify the Fe species in aerosols. The fitting of XAFS spectra coupled with micro-XRF showed that main Fe species in aerosols in Tsukuba were illite, ferrihydrite, hornblende, and Fe(III) sulfate. Moreover, soluble Fe fraction to total Fe in each sample measured by leaching experiment is closely correlated with the Fe(III) sulfate fraction determined by XAFS, suggesting that the presence of Fe(III) sulfate is primarily important for the supply of soluble Fe into the ocean. Another possible factor, total concentration of Fe(III) in the atmosphere in terms of the amount of supply of soluble Fe into ocean was high in spring due to the high concentrations of mineral dust in the period in East Asia, but this factor does not contribute to the amount of soluble Fe to a larger degree than the effect of Fe(III) sulfate. Thus, it was concluded that the most significant factor controlling the supply of soluble Fe in North Pacific can be the concentration of anthropogenic Fe species such as Fe(III) sulfate.


Vertical profiles of copper isotopic composition in the ocean

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Copper is an essential trace metal that shows a vertical recycled-scavenged profile in the ocean. To elucidate the biogeochemical cycling of Cu in the oceans, it is important to determine the profiles of Cu isotopes in the ocean. However, precise isotopic analysis of Cu has been impaired by the low concentrations of Cu as well as co-existing elements that interfere with measurements by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). We have developed a precise and simple method for determining the Cu isotopic composition of dissolved Cu in seawater. Dissolved Cu was preconcentrated using a Nobias Chelate-PA1 resin and purified using an AG MP-1 anion exchange resin. The concentration and isotopic composition of copper were measured using an Element 2 HR-ICP-MS and a Neptune MC-ICP-MS, respectively. Cu isotopic composition data were expressed as δ65Cu, where δ65Cu (%) = [(65Cu/63Cu)sample/(65Cu/63Cu)NIST SRM 976] × 103.

We have determined δ65Cu in the western North Pacific and Japan Sea. In the western North Pacific, δ65Cu values were +0.45–0.53‰ above the thermocline. Below the thermocline, δ65Cu values were increased to +0.49–0.71‰. In the Japan Sea, δ65Cu values were +0.48–0.57‰ above the thermocline, which were similar to that of the western North Pacific. Below the thermocline, however, δ65Cu values were lighter (+0.28–0.56‰) than that of the western North Pacific. We will also reveal the distribution of δ65Cu in the eastern North Pacific and central Indian Ocean. We are going to constrain biogeochemical cycles of Cu using δ65Cu and Cu concentration data. Our hypotheses at present is that δ65Cu above the thermocline is balanced by biological removal of light Cu and aeolian supply of light Cu, and that δ65Cu below the thermocline become heavy with the increase in AOU because of preferential removal of light Cu.

Influence of surface condition on data quality of U–Pb zircon dating

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U–Pb zircon dating using microbeam such as SIMS and LA-ICP-MS has played a pivotal role in geochronology. Many analysts empirically believe that accuracy and precision of microbeam analysis strongly depend on surface condition of analytical spots. Especially, existence of cracks within the analytical spots decreases quality of results, but there is no quantitative evidence that the crack decreases the data quality. In this study, we quantitatively discuss influence on the data quality from the surface condition of the analytical spots. AS3 and FC1 zircons collected from gabbroic anorthosites of the Duluth Complex, Minnesota, USA, were used in this study. Previous work reported that some grains in AS3 zircons yield discordant data due to Pb loss caused by thermal diffusion [1].

Observation of thin sections by optical microscope and electron microprobe reveals chloritization of amphibole in AS3, which suggests hydrothermal alteration. U–Pb analyses of some AS3 zircon grains yielded discordant data. The analytical spots that yield discordant data can be classified into (1) altered domains characterized by high contents of LREE and non-formula elements, such as Ca, Al, and Fe, and (2) domains containing undersurface cracks. In the case that analytical depth is close to the undersurface cracks, the second domains also show high LREE contents. When the cracks in zircon worked as channels of hydrothermal fluid [2], there are possibilities that some residuals of the fluid exist in the cracks and/or that areas around the cracks was altered by the fluid. Therefore, selection of the analytical spots for U–Pb zircon dating should be based on observation of cracks not only on the surface but also under the surface. When AS3 and FC1 zircon are used as U-Pb standard material, it is important to carefully choose analytical spots on the basis of the backscattered electron and optical microscope images for achieving more precise analysis.

Geochemistry of spinel-hosted amphibole inclusions in abyssal peridotite: Embedded evidence for melt-peridotite reaction process?

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Trace-element compositions of spinel-hosted amphibole inclusions (20-40 µm) were determined by using LA-ICP-MS to more throughly understand the melt-peridotite reaction.

Spinel-hosted hydrous minerals (e.g., amphibole and phlogopite) have been documented in ultramafic rocks from the ocean floor and ophiolitic complexes [1, 2]. They are commonly observed in dunite, troctolite and chromitite, to which formation the melt-peridotite reaction contributed significantly. However, the role of formation of the inclusions has been ever constrained well within the framework of melt-peridotite reaction. Arai et al. [1] pointed out that the mineral inclusions are formed from a melt enriched in incompatible elements, e.g., TiO₂ and Na₂O, and H₂O, produced by zone refining effects in the melt-peridotite reaction. Until now, trace-element compositions of the inclusions have been rarely examined [2, 3] due to difficulty in establishing their geochemical systematics because of complicated multi-scale uncertainties on the reaction mechanisms, such as melt and rock compositions and geological setting.

A core interval (70 cm) of the residual harzburgite cut by gabbro recovered from the Atlantis Massif, Mid-Atlantic Ridge 30°N shows inhomogeneous compositions caused by reaction with melt forming the gabbro [4]. Pargasitic amphibole inclusions in concentric spinel grains are only observed in the harzburgite near the gabbro contact (10 cm) where depleted residual harzburgite reacted with N-MORB-like melt beneath the ridge. Because the geological and petrological context is well constrained there as above, the pargasite geochemistry will give us a good reference for the systematics of relevant reaction and origin of inclusions. Together with trace-element data of spinel-hosted amphibole inclusions in reacted rocks, we discuss the significances of inclusions on the melt-peridotite reaction processes.


Mission invisible: residual mantle wedge contains phlogopite?

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It is often mentioned that arc basalts are highly depleted in high-field strength elements (HFSE), such as Nb, Ta, Zr and Hf. In the spidergram, which shows four types of primary magmas in the Mariana arc (Tamura et al., 2011; Tamura et al., submitted) (Fig. 1), it is worth mentioning that North West Rota-1 (NWR1) POB, which is the driest and least depleted primary magma type among the four, is not as depleted in Nb, Ta, Zr and Hf as are the other three varieties and contains about 4x more of these HFSE than primitive mantle and are comparable to their HREE contents. On the other hand, the differences in Nb and Ta contents between NWR1 POB and more depleted COB are much larger than those expected from the different degrees of melting. This is also the case for Pagan COB1 and COB2 and comparing Pagan and NWR1. Apparently, Nb and Ta decrease unusually when the fraction of melting increases or when primary magmas become more hydrous from POB through COB and COB2 to COB1.

When the melting conditions are ‘dry’ as is true for POB, phlogopite would not be present and Nb and Ta would become highly incompatible. It could be possible that highly depleted hydrous residual mantle wedge of the subduction zone could be phlogopite bearing dunite and harzburgite, which causes depletion of HFSE in wet and depleted arc magmas.

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Circulation effect: Response of precipitation $\delta^{18}O$ to the ENSO cycle in monsoon regions of China

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Based on an analysis of the relationships between the time series of amount-weighted mean annual $\delta^{18}O$ in precipitation ($\delta^{18}O_w$) and meteorological variables such as temperature, precipitation as well as atmospheric/oceanic circulation indices, it is recognized that the El Niño-Southern Oscillation (ENSO) cycle appears to be the dominant control on the interannual variation in $\delta^{18}O_w$ in the Monsoon Regions of China (MRC). Further analysis shows that the trade wind plays a role in governing $\delta^{18}O_w$ through affecting the intensity of the different monsoon circulations which are closely linked to the weakening and strengthening of the trade wind and gives the $\delta^{18}O_w$ different values at or over inter-annual timescales. The southwest monsoon (SWM) drives long-distance transport of water vapor from Indian Ocean to the MRC, and along this pathway increasing rainout leads to more negative $\delta^{18}O_w$ from Indian Ocean to the MRC, and along this southwest monsoon (SWM) drives long-distance transport of $\delta^{18}O_w$ and ENSO.

Achieving the synchronization between the $\delta^{18}O_w$ in the MRC and leads to less negative $\delta^{18}O_w$ value directly reflects the differences in influence the MRC and leads to less negative $\delta^{18}O_w$. Therefore, the $\delta^{18}O_w$ value reflects the differences in influence the MRC and leads to less negative $\delta^{18}O_w$. Therefore, the $\delta^{18}O_w$ value directly reflects the differences in influence between the SWM, which is strong when the SE trade wind is weak, and the SEM, which is strong when the SE trade wind is weak. In addition, the South China Sea Monsoon also transports local water vapor as well as plays a role in achieving the synchronization between the $\delta^{18}O_w$ and ENSO. The author thus terms the $\delta^{18}O_w$ rhythm in the MRC the “circulation effect”.

Particle-size dependent distribution of radiocesium in river sediments after the FDNPP accident

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It was reported that most of fallout radiocesium emitted by the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident stayed within 5 cm of surface soil layers [1,2]. Such accumulated radiocesium at the very surface on the ground is possibly being eroded into rivers by surface runoff, and finally goes into the Pacific Ocean. Particle size is an important factor in transportation of radiocesium in river systems. In this study, therefore, we investigated the dependence of radiocesium concentration on particle size and the distribution of particle size in river sediments.

River sediment samples were collected at 8 points in the Abukuma River and Kuchibuto River, which is one of the branches of the Abukuma River. River sediments were divided into 11 fractions with different particle sizes, > 2000 µm, 850 – 2000 µm, 500 – 850 µm, 250 – 500 µm, 125 – 250 µm, 63 – 125 µm, 40 – 63 µm, 20 – 40 µm, 10 – 20 µm, 2 – 10 µm and < 2 µm size fractions. Radiocesium concentration in each fraction was measured with γ-ray spectrometry using a planar type germanium semiconductor detector.

Smaller particle fractions contained a large amount of radiocesium possibly because of the following two factors. One is the specific surface area, and the other is the mineralogy of the sediments. Smaller particles have larger specific surface areas, providing more sorption sites for radiocesium. Also, a large amount of clay minerals, on which radiocesium is strongly sorbed, are contained in smaller fractions. On the other hand, the contribution of each particle-size fraction to radiocesium in bulk sediment is also affected by the mass distribution of sediment particles among different particle sizes as well as radiocesium concentration in each particle-size fraction. In this sense, the contribution of relatively large size fraction to total radiocesium concentration is not negligible in bulk sediment.

A study on adsorption mechanism of organoarsenic compounds onto ferrihydrite

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The inorganic arsenic compounds are cause of groundwater pollution in the world. In addition, organoarsenic compounds also have potential of the water pollution. It is important to know the adsorption structures of arsenic compounds to understand the migration of arsenic compounds in environments. In this study, adsorption structures of methyl and phenyl substituted organoarsenic compounds onto ferrihydrite, one of the most active adsorbents for anions in nature, were studied by the extended X-ray absorption fine structure (EXAFS) measurement and density functional theory (DFT) calculations.

Methylarsonic acid (MMA), dimethylarsenic acid (DMA), phenylarsenic acid (PAA), and diphenylarsinic acid (DPAA) were adsorbed on ferrihydrite at 25°C, pH 4 and 7. As K-edge EXAFS spectra of organoarsenic solution and adsorbed on ferrihydrite samples were collected by BL01B1 at S Pring-8 and BL-12C at KEK Photon Factory (PF).

The EXAFS spectra suggest that all organoarsenic compounds treated in this study form inner-sphere complexes with ferrihydrite regardless of bulky functional groups. The interaction energy analysis using DFT calculations indicate that the steric hindrance between organoarsenic compounds and surface functional groups of ferrihydrite dominate the adsorption structures and adsorption amounts.

Internal $^{238}$U-$^{230}$Th isochron method for dating young basaltic eruptions

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Dating of young (Late Pleistocene to Holocene) volcanic eruption gives valuable information in volcanology, environmentology, and archaeology. Although several geochronological methods such as $^{40}$Ar/$^{39}$Ar, (U-Th)/He, and $^{14}$C, and U-series disequilibrium, have been applied for dating, there exist many analytical limitations in these methods especially for young basaltic volcanics.

This study demonstrates the applicability of $^{238}$U-$^{230}$Th internal isochron methods for the determination of eruption age from young basaltic volcanics using chemically-separated groundmass phases. Groundmass phases of basaltic lava collected from Laguneta volcano, El Salvador, were separated into several fractions with different magnetic susceptibility, followed by leaching in hydrochloric acid solution. Hydrochloric acid solution congruently dissolves olivine, titanomagnetite, and phosphorous-bearing minerals; incongruently dissolves anorthite-rich plagioclase; and does not dissolve augite, albite-rich plagioclase, and alkali-feldspars in the examined groundmass phases. During acid leaching, the range of ($^{238}$U/$^{232}$Th) increased from 0.2 (unleached groundmass fractions) to 1.8 (leachates and residues). No, or little, preferential leaching between U and Th occurs by the acid-leaching treatment. Thus, the linear regression line obtained by leachate, residue, and unleached groundmass fractions can be regarded as an isochron, the slope of which indicates the eruption age. The $^{238}$U-$^{230}$Th internal isochron age for two individual samples gave an identical value within the error. Using all the fractions from two samples, the most precise $^{238}$U-$^{230}$Th isochron age was determined as 14 ± 1 ka (2σ). This age agrees with the degassing-induced external $^{235}$U-$^{230}$Th isochron age obtained by whole rock samples when the error is considered. This study also revealed that acid-leaching preferentially fractionates Ra/Th because of incongruent dissolution of plagioclase. Thus, $^{230}$Th-$^{226}$Ra isotope systematics cannot be used for acid-leached samples. The significance of this study lies in the development of precise geochronological method for any type of volcanics which erupted between ~3 and ~300 ky.
Characteristics and driving factors of surface water chemistry of Wujiang watershed

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The changes of water chemistry of rivers can reflect influence of anthropogenic activities on water environment in some extent. In order to understand the relationship between the spatial distribution of eco-environment of the watershed and the characteristics of water chemistry and geochemistry of rivers, firstly, the digital Wujiang watershed was built, and then the sub-watersheds were delineated, taking the sample points as sub-watershed outlets based on GIS. Secondly, using the function of spatial analyst of GIS, the statistical features of eco-environment (such as lithology and land use/cover) of each sub-watershed were calculated according to their respective classification. Finally, the correlation between the spatial distribution of lithology of the sub-watersheds and their corresponding \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of river water, the correlation between NO\(_3^-/\text{HCO}_3^-\), Cl\(^-/\text{HCO}_3^-\), SO\(_4^{2-}/\text{HCO}_3^-\) and anthropogenic activities respectively, and the correlation between the fraction of green vegetation of the sub-watershed and their corresponding flux of TDS (total dissolved solids) were analyzed quantitatively. The results justify that the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of river water is highly dependent on the lithologic feature of the watershed and indicate that anthropogenic activities are one of the main sources of NO\(_3^-\) and SO\(_4^{2-}\) of river waters, the output of TDS is highly dependent on the percentage of vegetation cover of the watershed.

Evaluation of kinetic effect on clumped isotope fractionation \((\Delta_{47})\) during inorganic calcite precipitation

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To date, published \(\Delta_{47}\)-temperature calibrations using different inorganic calcite precipitation and biogenic carbonates, as well as obtained by theoretical calculations, are not consistent. Here we present a set of \(\Delta_{47}\) data measured from inorganic calcites grown at well-controlled experimental conditions. We show that measured \(\Delta_{47}\) values are strongly influenced by pH during calcite precipitation. When pH is between 8.3 and 9.0, measured \(\Delta_{47}\) values \(1\) generally increase with decrease of temperature, \(2\) are not sensitive to the change of precipitation rate, and \(3\) are not sensitive to variation in ionic strength. The \(\Delta_{47}\)-temperature equation calibrated by our \(\Delta_{47}\) values for inorganic calcite grown at pH between 8.3 and 9.0 can be written as,

\[
\Delta_{47} = (0.0367\pm0.0033) \times 10^6/T^2 + (0.2743 \pm 0.0376)
\]

where \(\Delta_{47}\) values were reported in the absolute reference frame. The slope of our calibration line is very similar to theoretical line (0.0392, Schauble et al., 2006; Guo et al., 2009). If pH >10, the \(\Delta_{47}\) values for calcite grown at 5°C significantly drift from the \(\Delta_{47}\)-temperature line. In this case the comparison of \(\delta^{18}O\) and \(\Delta_{47}\) values of calcite grown at pH >10 to that grown at pH<9 indicates that every 1‰ depletion in \(\delta^{18}O\) values results in 0.0155‰ enrichment in \(\Delta_{47}\) values. We argue that any observed kinetic effect on carbonate clumped isotope fractionation is mainly due to isotopic non-equilibrium occurring in the solution during CO\(_2\)-H\(_2\)O (de)hydration and (de)hydroxylation.

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Geochronology and geochemistry of Early-Middle Triassic magmatism in the Argun Massif, NE China: Constraints on the tectonic evolution of Mongol–Okhotsk suture belt

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The Mongol–Okhotsk suture belt is located between the North Asian and the North China cratons and played an important role in the formation and tectonic evolution of eastern part of the Eurasian continent during Mesozoic. However, it remains debated whether the southward subduction of the Mongol-Okhotsk oceanic plate beneath the Argun Massif happened. In this paper, we undertook zircon U-Pb dating and geochemical data of the Early-Middle Triassic intrusive rocks in the Argun Massif which is bounded by the Mongol–Okhotsk suture belt to the northwest, with the aim of addressing the above-mentioned question.

Zircons from five representative intrusions in the Argun Massif are euhedral–subhedral, and display fine-scale oscillatory growth zoning in CL images, implying a magmatic origin. Zircon U-Pb dating demonstrates an Early-Middle Triassic magmatism in the Argun Massif, aged between 241 and 247 Ma. The Early-Middle Triassic rocks are composed of a suit of diorite, granodiorite, monzogranite, and syenogranite. They have SiO₂ = 57.71–72.86 wt.%, Mg# = 19–52, K₂O = 2.39–5.00 wt.%, and Na₂O = 3.28–4.28 wt.%. Chemically, they belong to the high-K calc-alkaline series. Moreover, they are characterized by enrichment in light rare earth elements (LREEs) and large ion lithophile elements (LILEs), and depletions in heavy rare earth elements (HREEs) and high field strength elements (HFSEs) such as Nb, Ta, and Ti. Their LREEs/HREEs ratios range from 9.68 to 21.56, and their δEu values vary from 0.61 to 1.31. Taken together, these Early-Middle Triassic intrusive rocks are similar to those from an active continental margin setting. Therefore, we conclude that the Early-Middle Triassic magmatism in the Argun Massif could be generated under an active continental margin setting related to the southward subduction of the Mongol-Okhotsk oceanic plate beneath the Argun Massif, which is also supported by the occurrence of the coeval porphyry Cu-Mo deposits such as the Erdenet Cu-Mo deposit in Mongolia and Taipingchuan Cu-Mo deposit in the Argun Massif, NE China.

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Theoretical calibration of Δ⁴⁷ values of ¹³C-¹⁸O clumps for carbonates

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Equilibrium clumped isotope distribution has been suggested as a new thermometer for various low temperature systems. With the help of a newly developed cluster-model based method for solids, we re-check equilibrium Δ values of ¹³C-¹⁸O clumps of those important carbonate minerals: calcite, aragonite, dolomite, nahcolite and magnesite. Although our method is totally different from the method of Schauble et al. (2006), our results generally agree with what Schauble et al. (2006) predicted except for nahcolite (NaHCO₃). For example, Δ values of ¹³C-¹⁸O clumps for calcite and aragonite at 25 C degree predicted by Schauble et al. (2006) were 0.41 and 0.43 (in per mil), our results are 0.436 and 0.445, respectively. It confirms that the results of calcite and aragonite are close to each other and there is only marginal difference between them. However, the result for nahcolite from Schauble was 0.41, as same as their result for calcite. Our result for nahcolite is 0.454 which is different from the result of calcite.

Furthermore, there are kinetic effects of isotope fractionation during phosphoric acid digestion of carbonates. The calculated kinetic isotope effect on ¹³C-¹⁸O digestion, we can obtain theoretical calibration lines for ¹³C-¹⁸O clumps of those important carbonate minerals: calcite, aragonite, dolomite, nahcolite and magnesite. If put our calibration line into the absolute reference frame diagram suggested by Dennis et al. (2011), our calibration line is far above the previous theoretical line and falls between the two experimental lines suggested by Caltech and Harvard groups. The slope of our calibration line is smaller than that of Caltech group but very slightly larger than that of Harvard group.

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Air-sea fluxes of dimethyl sulfide and acetone in the subtropical and equatorial Pacific Ocean

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Fluxes of dimethyl sulfide (DMS) and acetone between the ocean and the atmosphere were measured in the subtropical South Pacific Ocean and the equatorial Pacific Ocean in January-February, 2012. Vertical profiles of these gases were obtained above the ocean surface by measurements at 7 heights from 1 to 1400 cm with a profiling buoy aboard R/V Hakuho-Maru during the KH-11-10 and KH-12-1 (EqPOS) cruises. The concentrations of DMS and acetone in gas samples were monitored by a proton transfer reaction-mass spectrometry (PTR-MS). The concentrations of DMS and acetone in the surface seawater and air were continuously measured with PTR-MS during the cruises. The mean sea surface concentration of DMS in the subtropical ocean (2.1±0.5 nM) was slightly lower than that in the equatorial ocean (3.2±1.0 nM). The DMS fluxes substantially varied in the range of 3.6–13.1 and 0.1–18.9 mol m⁻² d⁻¹ in the subtropical and equatorial oceans, respectively. The magnitude of DMS fluxes was dependent of wind speed. The gas transfer velocities of DMS were calculated from the fluxes and the seawater DMS concentrations. We will discuss gas transfer velocities in comparison to previous studies. The air-sea fluxes of acetone will be also presented and discussed.

Partitioning of Nb between rutile and NaAlSi₃O₈-, NaCl- and NaF- aqueous fluids at 1-5 GPa and 300-600°C

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Rutile (TiO₂) has been proposed as an important host for high field strength elements (HFSE) such as Nb and Ta in high-pressure, moderate temperature metamorphic environments, including subduction zone systems. The observed depletion of HFSE in arc magmas can be explained if rutile is chemically inert with respect to aqueous fluids evolved during progressive metamorphism of subducted slab materials. However, both field observations and experimental studies [1] suggest that titanium, as well as HFSE can be soluble in aqueous fluids. Published experimental data were obtained by performing experiments at temperatures >700°C and pressures <2.5 GPa, conditions not entirely relevant to fluid loss in many arc systems. Here, we report new data that constrain directly the partitioning of Nb between fluid and rutile at 1 to 5 GPa and 300-600°C, conditions applicable to fluid evolution during the blueschist to eclogite transition.

We investigated systematically the partitioning of Nb between aqueous fluid and Nb-rutile (1wt% Nb) by adding albite (NaAlSi₃O₈), 10 and 20 wt % NaCl, and 4 wt % NaF to the fluid phase. The concentration of Nb in aqueous fluid was measured directly by using a hydrothermal diamond anvil cell and synchrotron X-ray fluorescence at the HPCAT 16-IDD beamline at the Advanced Photon Source.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Pressure (GPa)</th>
<th>Temperature (°C)</th>
<th>Nb Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% NaCl</td>
<td>1.2-2.8</td>
<td>300-700</td>
<td>9-23</td>
</tr>
<tr>
<td>20% NaCl</td>
<td>1.7-4.7</td>
<td>300-600</td>
<td>24-86</td>
</tr>
<tr>
<td>NaAlSi₃O₈</td>
<td>1.0-5.8</td>
<td>300-600</td>
<td>100-1050</td>
</tr>
<tr>
<td>4% NaF</td>
<td>3.0-6.5</td>
<td>300-500</td>
<td>260-1075</td>
</tr>
</tbody>
</table>

Our data indicate that dissolved NaF and albite, relative to pure water and NaCl, have a much greater effect on enhancing Nb concentration and transport in dense, moderate temperature, aqueous fluid. Our findings are consistent field studies such as [1] that document HFSE mobility in aqueous fluids evolved during the blueschist to eclogite transition.

Properties and structural role of iron in silicate melts and glasses

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Iron is an important element to probe the properties and the structure of silicate melts. In earth science most of lava contain more than 10% of iron whereas the proportion is much smaller in industrial materials. Iron usually occurs in two different valence states (Fe2+ or Fe3+), and three coordination: 4, 5 and 6 for these different redox states. Thus, the influence of iron oxide on the melt properties is complicated. Consequently, the redox ratio of silicate glasses and melts is an important parameter which role must be properly studied to understand the physical and chemical properties of these materials.

The coordination of iron may evolve as a function of the redox state. These changes are due to the fact that iron is essentially present in the form of Fe3+ in tetrahedral position at lower temperatures whereas it mainly occurs as Fe2+ in 6-fold coordination at higher temperatures. These changes in the iron coordination may influence the short range order around network modifier, such as Na or Ca. Our goal is to understand the importance of those coordination modifications caused by the change in iron redox.

X-ray absorption spectroscopy experiments are very valuable to determine short-range order. It should allow us to study the iron valence and coordination, as well as the sodium and calcium environment. However this technique is not always accessible. Therefore, other experimental methods must be used to study the network modifications such as Raman spectroscopy and electron microprobe.

We focused our work on the changes which happen in the glass during the transition between different redox states. Especially with regard to the network structure and the local environment of network-modifier elements.

Temporal variations in the composition and age of terrestrial organic carbon transported by the Yellow River

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The Yellow River is the World’s highest turbidity major fluvial system, delivering over $1 \times 10^9$ t of sediments annually into the Chinese marginal seas, accounting for ~7% global sediment flux to the ocean. Organic carbon carried by the Yellow River therefore may play a significant role in the global and regional organic carbon cycle.

The focus of the present study is to develop an understanding of the sources, composition and age of terrestrial organic carbon that is carried by the Yellow River and supplied to the adjacent Bohai Sea and Yellow Sea. Near-surface suspended particulate matter samples were collected nearby the Lijing Station, ~50 km upstream of the river mouth (Dongying), as part of a sampling campaign between June 2011 and June 2012 in order to assess seasonal variations in fluvial supply. In addition to bulk properties, the abundance and carbon isotopic composition of source-specific biomarkers (fatty acid & alkanes) were measured.

The concentrations of higher plant-derived long-chain (≥ C20) n-alkanes, n-fatty acids and particulate organic carbon (POC) co-varied with total suspended solid (TSS) concentrations, with peak abundances during summer and early autumn, indicating plant-derived organic carbon is controlled by the overall flux of terrestrial sediments, which in turn is influenced by flood events and human activities.

POC in the Yellow River exhibits relatively uniform δ13C values (-23.94 to -24.37‰), and old radiocarbon ages (4000 to 4600 14C years). Radiocarbon ages of short-chain (C16, C18) fatty acids were variable but generally modern (from 560 years to greater than modern), suggesting they are sourced from fresh terrestrial debris, but more likely from aquatic productivity during warm and low-turbidity periods. In contrast, long-chain fatty acids display a relatively narrow and pre-aged range from 1550 to 2080 years.

These results, and associated molecular and isotopic information, indicate that the aged OC – likely sourced from soils on the Chinese loess plateau within the drainage basin – contributes significantly to the suspended load of the Yellow River.

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Linking kimberlite magmatism, transition zone diamonds, and subduction processes

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The presence of diamonds with transition zone (TZ) inclusion parageneses in a growing number of kimberlites worldwide is generally considered evidence for an ultradepth origin of kimberlites. However, combined geochemical and experimental evidence, including mantle redox constraints, suggests that kimberlite magma formation is best explained by volatile-flushed melting of refertilized depleted upper mantle domains.

We analysed the Sr-Nd-Hf isotope compositions of fresh hypabyssal kimberlites from the 75- to-55 Ma Lac de Gras (LDG) field of the central Slave craton that contains TZ diamonds. The LDG kimberlites show the most extreme Nd-Hf isotope decoupling reported from global kimberlites. Isotopic modelling suggests that the steep-angled array in Nd-Hf isotope space is best explained by mixing of convecting upper mantle-derived CO2-rich melt with minor amounts of alkali silicate melt derived from an isolated mantle reservoir with extremely unradiogenic Hf. Our data indicate that OIB-type material stored in the transition zone for >2 Gyr can be the source of the alkali silicate melt component. Given that the nearby 170 Ma Jericho kimberlites contain neither TZ diamonds nor anomalously unradiogenic Hf, we suggest that onset of fast and steep subduction along the western margin of North America at 100 Ma caused significant entrainment of ancient TZ material into the upper mantle beneath the region. Recycled ancient OIB-type material partially melted during the subduction-triggered upward mantle flow, and locally refertilized the depleted upper mantle. Subsequent CO2- and H2O-flushed redox melting of refertilized domains gave rise to kimberlite magma formation beneath the thick cratonic lid in the LDG area starting at 75 Ma. Model calculations indicate that ancient TZ diamonds could have been brought to the Slave craton base by vigorous mantle flow near a subduction zone within <25 Myr, such that they were available for sampling by the ascending upper mantle-derived LDG kimberlite magmas at 75 Ma [1].


A Possible Route to K+-Enriched Aqueous Solutions on Early Earth

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All known living organisms have a K+-rich intercellular medium, while usually existing in a Na+-enriched environment [1]. High K+ concentrations are required for the proper function of numerous essential enzymes and ribozymes [2]. This difference between cation concentrations is translated to potential difference used for energy storage and signalling. Most of the natural terrestrial environments are known to be enriched in Na+ due to its higher abundance and high solubility of its salts. The Na+/K+ mole ratio inside living cells varies around 1/10, which is roughly the opposite ratio of these ions in seawater (47/1). In this work we show that one of the processes leading to the enrichment of groundwaters in K+ can occur during acid weathering of Aluminium rich clays and zeolites and the fractional secondary precipitation of alunite and Na-alunite.

Zeolites and montmorillonites were treated by acidic (0.1-1M H2SO4) solutions (K+/Na+ mole ratio 1/5) at temperatures 20°-50°C. The clay/acid mixtures were left to evaporate. During the drying process octagonal crystals were formed from coalescent brines on the surface of the clays. The crystals were identified by X-ray diffraction and ICP analysis as KAl(SO4)2. The remaining interstitial brine was enriched in Na+ and close to saturation with respect to NaAl(SO4)2. Fast washing from the final mixture surface leads to the enrichment of K+ in the formed solution by orders of magnitude depending on pH, temperature and a mineral type. This proposed scenario leads to environments rich in potassium and can also be applied for accumulation of other prebiotic components, such as phosphate and small organic molecules. We suggest that acid weathering could be a process to accumulate essential components for the chemical origin of life.

How much magmatic water is transported by volcanic gases?

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Gases sampled from volcanic fumaroles and from the surface of lava lakes and lava flows are characterized by temperatures from boiling point of water up to 1100°C. The main component of volcanic gases is water vapor with concentrations from ~50 to 99 vol%. The fraction of magmatic water in volcanic gases is estimated using the isotopic composition of volcanic vapor. For the highest temperature fumaroles of subduction-type volcanoes D/H ratios on average ~ -25‰ (V-SMOW) and ¹⁸O/¹⁶O are close to the corresponding values of the whole rock, usually from +6‰ to +9‰. In many cases volcanic vapors of arc volcanoes with t>800°C are represented by almost pure magmatic water. However, there are numerous exceptions from this rule when a >800°C volcanic gas is a mixture of magmatic water with up to 50% of meteoric or seawater vapors. Most of the arc fumarolic gases demonstrate a single trend of mixing between magmatic and meteoric end members in their chemical and isotopic compositions. Much more complicated are cases related to volcanic gases from hot spot and rift volcanoes with magmas much less water abundant that arc magmas. Low and medium-temperature fumaroles of Kilauea (Hawaii) and Sierra Negra (Galapagos) discharge gases with a low content of water vapor (50-70 vol%) but all these vapors apparently have meteoric origin and thus the real proportion of magmatic water and its isotopic composition in gases of these hot spot volcanoes is impossible to determine. The new data on the high-temperature (> 1000°C) volcanic gas from a hornito of the Erta Ale lava lake (Zelenski et al., submitted) make possible to estimate the isotopic composition of magmatic water for this continental rift volcano. The Erta Ale volcanic vapor derived from the liquid lava lake seems to be about half diluted by meteoric water and has the isotopic composition between that of local meteoric water and water with δD=-60‰ if to accept δ¹⁸O=+6‰, like in the Erta Ale whole rock samples. However, this suggestion assumes the absence of the oxygen isotope exchange between CO₂ and H₂O during sampling when the ~1:1 H₂O+CO₂ mixture is cooling from the vent to condensate temperature.

Important factors for geochemical research of stream sediments near storm water outflow sites

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Urban storm sewer system is an important pathway of transfer of contaminants to the hydrosphere. Presuming that each storm water outflow (SWO) can increase the content of potentially harmful chemical elements (PHE) in stream sediments, matched pairs of samples can be taken upstream and downstream from SWO. Water flow rate differences lead to variability of lithological composition (from clay to sand) and geochemical changes even within short distance. It is useful to find out the advantageous grain size fraction for revealing the geochemical changes due to influence of SWO.

Thirty nine samples of Neris river sediments including 12 matched pairs of samples near SWO sites of Vilnius city were taken. The contents of Pb, Zn, Cu, Ni, Cr (PHE) and rock forming elements Al, Ca, Na, K, Fe, Si, P, S, Ti, Mn were determined in the bulk fraction (<2.0 mm) and fractions <0.1 mm, 0.1-0.25 mm, 0.25-0.50 mm by x-ray fluorescence. In most samples the fraction 0.1-0.25 mm (average is ~57%) and <0.1 mm (30%) prevails. In sequence of fractions <0.1 mm, 0.1-0.25 mm, 0.25-0.50 mm the contents of most elements decrease due to dilution by quartz and plagioclases. Using Wilcoxon matched pairs test for the bulk fraction the differences between samples upstream and downstream from SWO are insignificant for all 5 PHE, meanwhile for the <0.1 mm fraction they are significant for Pb, Zn and Cu. The increase of Cr and Ni contents is insignificant, because they are not the main in pedogeochmical anomalies of Vilnius.

Analysis of <0.1 mm fraction seems to have advantages in comparison with the bulk fraction <2 mm for indicating places of storm water outflow. For refinement of results, not only enrichment factors should be calculated by normalising to clay-related (Al, Mg, K, Ti) or biophylic (S, P) elements, but also the dilution factor by sand (Si) taken into account.
NanoSIMS Pb/Pb dating of tranquillityite in lunar basalts

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Ion microprobe U-Th-Pb geochronology was first carried out three decades ago [1-2] to date phosphates and Zr-rich minerals from lunar samples, but was hampered by the limited mass resolution of the instrument. Subsequent analytical developments improved the accuracy and precision of in-situ Pb isotope measurements. In lunar samples, in-situ U-Pb dating has mostly been focused on zircon (e.g., [3] and refs therein), which occurs in rock types mainly representing the lunar highlands [3], while it is rare in mare basalts in which U and Th, are mostly hosted by baddeleyite, zirconolite and tranquillityite. This latter group of minerals can also yield precise and accurate Pb/Pb ages [4-9]. However, their small sizes often pose serious challenges to application of in-situ dating techniques.

We have used the NanoSIMS 50 at the University of Rennes 1 to carry out high-resolution Pb/Pb dating in tranquillityite in mare basalts. The 120-140 pA primary O beam produced ~3 µm spots. We obtained average 207Pb*/206Pb* dates of 3713 ± 8 Ma, 3769 ± 8 Ma and 3736 ± 10 Ma for samples 10044, 75055 and 74255, respectively, which occurs in rock types mainly representing the lunar highlands [3], while it is rare in mare basalts in which U and Th are mostly hosted by baddeleyite, zirconolite and tranquillityite. This latter group of minerals can also yield precise and accurate Pb/Pb ages [4-9]. However, their small sizes often pose serious challenges to application of in-situ dating techniques.


Evidences of paleoproterozoic metamorphism in the NW region of the Quadrilátero Ferrifero area, Minas Gerais, Brazil: Implications for gold mineralizations

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It was characterized a paleoproterozoic medium-grade metamorphism related to the gold mineralizations in the NW area of the Iron Quadrangle (Quadrilátero Ferrifero), in Minas Gerais State, Brazil. The gold ores are hosted by sericite-chlorite quartz schist from the upper metamodified unit of the Rio das Velhas Supergroup. These rocks are metamorphosed under transitional greenschist-amphibolite facies conditions and comprise garnet + staurolite + cummingtonite, biotite + chlorite + plagioclase + quartz; the metamorphic peak is at ca. 600ºC and 6.6 kb. The ore consist of arsenopyrite, pyrite, pyrrhotite and free gold in a gangue made of quartz, carbonates, graphite and oxides (hematite, magnetite and ilmenite). The age of the metamorphism was characterized by Sm-Nd ages for garnet-whole rock and Rb-Sr whole rock isochron with an ages around 2.2 Ga. The 1.9 Ga Rb-Sr age of biotite suggest that high geothermal gradients were sustained for a long period of time. The ore minerals are dated by Rb-Sr and Pb-Pb methods, which give an ages of 2.15 and 2.0 Ga. Rb-Sr applied to hydrothermal sericite–whole rock pair, yielded an age of 1928 ± 2.6 Ma. The 2.1-2.0 Ga ages could be related to the first stage of mineralization at 600 ºC. The age of 1.9 Ga could be related to the boiling episode that occurs at ~340ºC. Pb, Sr and Nd isotopic compositions of the ore minerals suggest that the hydrothermal fluids represents mixing between several reservoirs, like the mantle, lower and upper continental crust. The metamorphism must have sustained elevated crustal geotherms for at least 100 Ma, promoting hydrothermal fluids circulation during the orogenic time.
Mo-W-Re-Au-Cu partitioning between vapor, brine and felsic melt: Super-solidus to sub-solidus

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The exsolution of metal-bearing “proto-ore fluids” from magmas initiates at super-solidus conditions and continues throughout cooling and decompression to solidus conditions for the parental magma. The range of exsolution conditions for a particular magma will affect the efficiency by which each ore metal is removed from the melt, the metal ratios in the exsolved fluid(s), the mass of metals available for transport, and ultimately the grade of the deposits.

Experiments performed at a range of P-T conditions across the solidus for a given magma composition provide insight into the behavior of these metals that is not readily accessible by study of natural samples. We have performed exploratory experiments to investigate the effect of the super-solidus to sub-solidus transition on metal partitioning between melt and volatile phases under ore-mineral saturated conditions. These experiments examine Mo-W-Re-Au partitioning, and wolframite-molybdenite solubility, at super-solidus (800 °C) experiments examine Mo- W-Re-Au partitioning, and sub-solidus transition on metal partitioning between melt and volatile phases under ore-mineral saturated conditions. These data are consistent with fractionation of Mo from W across the super-solidus to sub-solidus transition. The impact of the transition is more pronounced for W (Dv/m = 11 ± 5 and 210 ± 120) compared to Mo (Dv/m = 10 ± 4 and 50 ± 25) as the temperature drops from 800°C to 725°C. These data are consistent with fractionation of Mo from W across the super-solidus to sub-solidus transition. The molybdenite- and wolframite-saturated fluids have W/Mo ratios that increase from 20 to 30 to 60 in the brine and 15 to 25 to 50 in vapor, for 800°C-100MPa to 725°C-100MPa to 700°C-75MPa, respectively. While these results are tentative, new experiments are in progress that include Mo, W, Re, Au, and Cu. These new experiments and new data analysis techniques will provide further insight into the effect of the super-solidus to sub-solidus transition on the composition and ore-mineral solubility limits of proto-ore fluids.

The silicon isotope record of early silica diagenesis

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During diagenesis, silica is converted to quartz through dissolution-reprecipitation reactions which are likely influenced by the silica isotope record of early stages of silica diagenesis that are hosting the youngest products of the incipient stages of silica diagenesis found to date.

High δ30Si values of 2.26 ± 0.18 ‰ (n = 5) and 1.97 ± 0.06 ‰ (n = 4) characterize two bulk porcelanite (opal-CT) layers found in two drill cores from Maude Rise and the Southwest Indian Ridge, respectively. Bulk δ30Si values of surrounding siliceous oozes are lower and range between -0.34 ± 0.08 ‰ (n = 4) and 0.60 ± 0.08 ‰ (n = 7), and 0.16 ± 0.08 ‰ (n = 4) and 1.45 ± 0.11 ‰ (n = 6), respectively.

Within these types of siliceous sediments, diatoms constitute both the compartment most prone to dissolution and heaviest in δ30Si consistent with [1]. Their dissolution together with isotope fractionation through rapid precipitation of inorganic opal (opal A’) during the ascent of pore fluids can produce isotopically heavy diagenetic fluids.

From these fluids porcelanite is precipitated only in narrow ranges of the host sediment characterized by extremely low detrital mineral contents.

High-spatial resolution analyses along profiles through two porcelanite layers by US-LA-ICP-MS show opposing trends of δ30Si and Al/Si ratios and indicate a kinetic control on the isotope fractionation factor, varying in response to the chemical composition of the fluid.

We identified processes of fluid generation, isotope fractionation, and chemical controls on precipitation during early stages of silica diagenesis that can well be extrapolated to conditions of ancient chert formation. The understanding of these processes can help discerning diagenetic fingerprints from source signals in the silica isotope record of chert.

U-Pb, Lu-Hf and Sm-Nd isotope systematics during polymetamorphism in the Ancient Gneiss Complex, Swaziland

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This study aims to resolve some of the potential complexity associated with Archaean polymetamorphic gneiss terranes, with specific application to high-grade paragneisses from the Ancient Gneiss Complex (AGC) in Swaziland. Archaean zircons and monazites which have experienced multiple growth and/or alteration episodes, typically display a complexity in their zonation and U-Pb ages which is near impossible to resolve. However, Gerdes & Zeh [2] showed that the radiogenic Hf content of zircon, for example, remains constant during alteration, and changes only during new zircon growth; providing a robust tool to constrain the exact number of metamorphic cycles a rock has been through. The Sm-Nd system could provide a similarly useful tool. Monazite, allanite, apatite, rutile and titanite are U, Th and light-REE bearing phases, making them highly amenable for Sm-Nd and U-Pb isotope analysis [1]. This study represents a first attempt at investigating the simultaneous behaviour of the U-Pb, Lu-Hf and Sm-Nd isotope systems in accessory phases during polymetamorphism, by in situ LA-MC-ICP-MS analysis.

We investigate metasedimentary granulites from two separate, spatially related areas of outcrop in south-central Swaziland, which were subjected to multiple high-grade events throughout the Mesoproterozoic [3]. Zircons and monazites from these gneisses are particularly interesting in terms of the complexity in their zonation and U-Pb ages, with dominant age peaks at 3.51 Ga, 3.43 Ga, 3.40-3.39 Ga, 3.35 Ga, 3.33 Ga, 3.23-3.21 Ga, 3.18 Ga, 3.16 Ga, 3.11-3.07 Ga, and 2.99 Ga. The U-Pb, Lu-Hf and Sm-Nd isotope record in these grains may inform on: (1) the provenance of sediments from the south-eastern Kaapvaal Craton and the nature of the Archaean/Hadean hinterland; (2) the number of metamorphic episodes recorded; and (3) Archaean geodynamic processes during key events associated with early lithosphere assembly and crustal differentiation.


Timing of ultra-high temperature (UHT) metamorphism and formation of incipient charnockites in the Kerala Khondalite Belt (KKB), southern India

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The Kerala Khondalite Belt, also known as The Trivandum Block (TB), makes up the southernmost tectonic unit of the Indian Subcontinent and the southern extension of the microcontinent Azania. The TB is dominated by high-grade metasedimentary rocks typically either grt-bt felsic gneisses (locally referred to an leptynites) and graphite-bearing grt-crd-sill gneisses (khondalites). The leptynites and khondalites, together with a variety of igneous rocks, have been metamorphosed to granulite facies. Metamorphic conditions vary, with the lowest pressures and temperatures in the centre of the block (5 kbar, ~750°C), and a systematic increase to the north and south up to 8-9 kbar and <1000°C. Charnockites within the Trivandum block typically form large-scale, orthopyroxene-bearing granitic bodies, such as those seen in the Nagercoil Block at India’s southernmost tip. However the appearance of incipient charnockites is more enigmatic, forming metre-scale “patches” within host leptynites, one classic locality being near Kottavattom [1].

Charnockitisation in these rocks is identified as a late stage process related to fluid migration through the host rocks, resulting in some of the youngest ages for accessory phases in the KKB. SHRIMP U-Pb data for both zircon and monazite in the host leptynite and incipient charnockite patches, combined with rare earth elements (REE) in zircon, monazite and garnet have been used to investigate the timing of charnockitisation in relation to the UHT metamorphism in the region.

Determination of strontium-90 in seawater using TODGA chelating resin

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Strontium-90 has been observed maximum values at late 1950s, which originated global fallout from nuclear weapons tests, and gradually reduced to about 1mBq/L in the Pacific Ocean (Pavinec et al., 2012). The accidents of the Fukushima Daiichi Nuclear Power Plant in Japan and the leak of contaminated water released various radioactive nuclides. Casacuberta et al. (2012) estimated that amount of Sr-90 release to the sea based on the observed Sr-90/Cs-137 ratio and Cs-137 by modeling data was 90 - 900 TBq. However, Sr-90 data are limited because of its complicated analytical procedure. Determination of Sr-90 in seawater generally requires preconcentration of Sr and separation from Ca and other beta emitters. In this study, rapid and robust purification technique for the daughter radionuclides yttrium-90 of Sr-90 using TODGA chelating resin (Eichrom) without separation of Sr from Ca. TODGA resin shows high distribution coefficient in high HCl and HNO₃ concentrations.

Sr in seawater (20L) was preconcentrated by oxalate coprecipitation. Precipitates was decomposed to carbonate at 550°C and dissolved in HCl and conducted Fe hydroxide coprecipitaion. After 2 weeks for ingrowth of Y-90, sample was conducted Fe hydroxide coprecipitaion. Precipitate was filtered and redissolved in 7 mL of 12M HCl. Sample solution was flowed to the column combined anion exchange resin (3mL) and TODGA resin (2mL). Most of seawater matrix such as Sr, Ca and Mg were removed by Fe hydroxide coprecipitaion and easily eluted 8M HCl from TODGA resin column. Fe and Bi were adsorbed to anion exchange resin. Pb and Bi were also eluted in 8M HCl fraction. Y was eluted by 20 mL of 0.1 M HCl. Y-90 was measured by low background gas flow proportional counter (Canberra LB-4100).

This analytical procedure was applied to seawater from the Pacific Ocean near the Japan Islands in January 2013. Averaged surface Sr-90 concentration was 0.95 ± 0.12 mBq/L, which is comparable to that before the accidents.

Regional modelling of Saharan dust

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The Sahara desert in northern Africa is the world’s largest source of dust aerosol. Regional-scale models help to understand processes involved in dust emission, transport and deposition, and are suited for comparisons with results of field studies like the SAharan Mineral DUst experiment (SAMUM) that aimed at improving the estimates of Saharan dust radiative forcing, or at understanding of dust deposition in the oceans. Models of modern atmospheric dust still often show considerable deviations from observations. One cause can be inadequacies in simulated meteorological fields that are used to compute dust emission fluxes. In contrast to global-scale dust models, regional dust models are expected to better reproduce individual dust events due to their higher grid resolution. Still, the representation of dust emission events that are related to precipitation events (haboobs, density currents) is problematic at grid resolutions that require parameterization of wet convection processes. New remote sensing products, together with the observations from recent field studies promise an improved understanding of dust regimes and are expected to lead to considerably improved dust models. We summarize findings of recent multi-year regional dust model studies and discuss open questions.
The halogen (F, Cl, Br) budget of continental granitoid plutonic rocks

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The main goal of this study is to decipher the contribution of various volatile-bearing minerals to the whole-rock halogen (F, Cl, Br) budget of continental granitoid plutonic rocks and how this budget is governed by primary and secondary minerals. For this purpose, we investigated various granitoids with different volatile-bearing silicate mineral assemblages: (1) hornblende + biotite, (2) only biotite and (3) biotite + muscovite. Furthermore, accessory apatite is present in all samples, whereas fluorite and titanite occur only sporadically.

Halogens (F, Cl, Br) were extracted from the whole-rock powders by Pyrohydrolysis and subsequently analyzed by Ion Chromatography. Volatile-bearing minerals were analyzed for F and Cl by means of Electron Microprobe Analysis and for Br by Total Reflection X-ray Fluorescence.

All the investigated rock samples lie in the range of 500-3000 µg/g F and 50-900 µg/g Cl, respectively. In several samples, F and Cl contents of the whole-rocks roughly correlate with the halogen contents of apatite, biotite and mica with the presence of fluorite. Br in the whole-rock powders is always <1 µg/g and quantifiable Br concentrations were only found in few hornblende and apatite separates.

Importantly, detailed calculations of the whole-rock halogen budget (based on modal analysis) show strong misfits for many samples and indicate that appreciable amounts of F and Cl are not incorporated in the minerals mentioned before. Indeed, detailed X-ray mapping and short-term leaching experiments (2 minutes) confirm that significant amounts of F and Cl are present (1) in tiny secondary mineral phases, (2) in fluid inclusions and (3) potentially located along grain boundaries. These cannot be accounted for budget calculations based on modal amounts of the various minerals.

Thus, our study shows that great care has to be taken when using the halogen contents of whole-rocks for petrogenetic models, since significant amounts of halogens in whole-rocks might be of secondary origin.

U-Pb geochronology of detrital zircons from metasedimentary rocks from Formation of Desejosa, Serra do Marão, Portugal

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The Serra do Marão area is located in the Central Iberian Zone and is dominated by an Ordovician sequence that rests on parallel unconformity on Cambrian/Neoproterozoic metasediments, belonging to Group of Douro. Two samples were collected from the upper formation of this Group (Formation of Desejosa): 1) a metapsamite from the top of this formation, which is characterized by a succession of metasiltitic and phyllic layers, and 2) an intraformational metaconglomerate. The U-Pb geochronological data obtained in detrital zircons by Laser Ablation-Quadrupole-Inductively Coupled Plasma Mass Spectrometry will help to constrain their maximum depositional age.

The U-Pb data set (52 detrital zircons with 99-107% and 33 detrital zircons with 85-103% concordant ages for metaconglomerate and metapsamite, respectively, is dominated by Neoproterozoic ages (84.6 % and 57.6 %), but there are few Cambrian (9.6 % and 9.1 %) and Paleoproterozoic (5.8 % and 3.0 %) ages. Mesoproterozoic detrital zircons are also present (6.1 %) in the metapsamite. Furthermore, a cluster of Ordovician ages in the metapsamite (24.2 %) yield a concordia age of (465 ± 16 Ma), which may reflect some Pb loss induced by the Early Ordovician felsic volcanism (470.1–474.6 Ma) in the area.

The detrital zircon population of both samples record a long-lived Neoproterozoic magmatic episode, probably located near or at the northern Gondwana margin. However, the contribution of other sources containing Mesoproterozoic (1151–1088 Ma) and Paleoproterozoic (2257–1821 Ma) zircons must be considered. The U-Pb concordia age suggest a maximum depositional age of 522 ± 26 Ma for the metaconglomerate and an preliminar interval from 537 ± 22 Ma to 516 ± 25 Ma for the metapsamite.

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U-Pb, Nd-Sr and geochemical fingerprints of granitic magmatism inside the Paleooproterozoic Mineiro belt, Southern São Francisco Craton: Evidence from the Ritápolis batholith

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The Mineiro belt (2.45-2.00 Ga) was created through accretionary arcs, ocean closure and eventual continent-continent collision. We document the case of the Ritápolis batholith (RB) – for which the U-Pb and Nd-Sr signatures and geochemistry provide new insights for the evolution of this belt. Dikes of the RB truncate the rocks of the so-called Resende Costa (2.36-2.33 Ga) arc. RB rocks vary from equigranular (fine-medium to coarse grained) to porphyritic with fenocrystals of plagioclase and microcline, showing igneous banding and different types of xenoliths (amphibolite, diorite, gabbro). LA-ICPMS U-Pb zircon dates yielded a crystallization age of 2149 ± 10 Ma (MSWD = 0.8) whereas the analyses from metamorphic rims yielded a lower intercept age of 662 ± 65 Ma, in agreement with the petrographic evidence. Seven Sm-Nd T DM ages fall between 3.5-3.6 and 3.1-3.3 Ga with -4.9 to -7.7 \( \varepsilon_{Nd}(t) \) values, suggesting that Archean protholiths participated in magma genesis. The RB samples show calc-alkaline and peraluminous to light metaluminous signatures, although a few ones resemble trondhjemites. The observed gaps between the high- and low K2O phases may be explained either by coeval rocks derived from different batches of at least two magma sources. High- and low K2O phases show roughly similar chondrite-normalized REE patterns, but with peculiar features (e.g., strong negative Eu anomalies for the high K2O group like evolved calc-alkaline rocks). This group also has low fractionated patterns in spider diagrams with enriched ratios when one considers the incompatible elements (e.g., Nd, Sm, Dy, Y, Yb and Lu). We conclude that the RB melts were derived in continental arc at 2150 Ma, placed opposite to the Serrinha intra-oceanic arc (2.23-2.20 Ga), as supported by geologic, isotopic and tectonic correlation.
Environmental fate and impacts of ceria nanomaterials: Distribution, transformation and bioaccumulation within aquatic mesocosms

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Ceria (CeO2) NPs are largely used as oxidation catalysts, gas sensor, polishing materials, but also as UV absorber. Their attractiveness comes from the high oxygen storage capacity related to the easy Ce(III)/Ce(IV) redox cycle. The presence of Ce(III) within the structure of CeO2 NPs enhance reactivity towards living organisms (prokaryotic and eukaryotic cells). Within the ANR-P2N MESONNET project, we determined the behavior of CeO2-based nanoparticles (NPs) within aquatic mesocosms simulating a pond environment. Another challenge was to work with NPs contamination representative of concentrations expected in natural aquatic environments. Consequently, NPs were chronically applied to water column (0.1 mg L-1 per injection). After 4 weeks, we determined the distribution of Ce in water, sediments and biota, speciation with X-ray absorption spectroscopy and oxidative stress in organisms was measured. Over time, NPs tend to heteroaggregate and accumulate at the surface of sediments. A partial reduction of Ce from oxidized CeO2 NPs was observed in the sediment. Bioaccumulation of major Ce(III) was also detected in digestive gland of pond organisms (snail, Planorbarius corneus) and correlated with a significant oxidative stress. In addition, using two kinds of CeO2 NPs for experiments (organic-coated CeO2-NPs used as paint additives (Nanobyk®), and “bare” CeO2-NPs (Rhodia®), we highlighted the influence of CeNPs surface formulation on their fate into mesocosms and their reactivity towards organisms.

Effect of solution supersaturation and presence/absence of seeding crystals on the precipitation kinetics of celestite and strontianite

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In general, precipitation kinetic experiments allow us to determine parameters such as critical saturation index (SI_for)_nucleation, rates of precipitation (R_precip) and induction time (t_ind) of nucleation. The objectives of this study follow a two-side approach: First we quantify the precipitation kinetics of the isostructural minerals celestite and strontianite under comparable R_precip extending the work of [1]. In MFR experiments, equimolar solutions of SrCl2 and Na2SO4 or Na2CO3 in 0.1M NaCl (background electrolyte) were fed through separate inlets in the reactor (v_outflow = 0.6 ml/min). Solution composition was monitored via ICP-OES and IC. R_precip of Celestite were calculated using the mass-balance equation to be ranging from 4*10^-9 to 20*10^-9 mol/(m2s) for SI's from 0.2 to 1.4, respectively. Plotting R_precip vs. SI's showed a parabolic trend suggesting a surface controlled precipitation mechanism at low SI and 2-D nucleation at higher SI. The SI_crit was found to be at 0.5 for SrSO4. t_ind between mixing of solutions and formation of the first cluster/colloid were determined by laser-induced breakdown detection (LIBD) in the absence of seeding material. t_ind decreased with increasing SI and two linear regressions could be performed with a change of slope at SI ~1.1. This SI is considered as the threshold for the transition between homogeneous and heterogeneous nucleation. The precipitation kinetics of celestite and strontianite will be compared and discussed with respect to nucleation mechanisms and metal uptake.

Elemental sulfur biomineralization and preservation in glacial sulfide springs

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Microbial activity can control the abundance and distribution of sulfur species in environments far from chemical equilibrium, including the precipitation of intracellular and extracellular elemental sulfur in association with organic structures such as surface coatings, cell surfaces, filaments and sheaths. However, the potential for the generation and preservation of S 0 mineral deposits that could serve as biosignatures of microbial sulfur cycling has not been extensively investigated. We will present a combination of synchrotron based x-ray spectroscopic, Raman, and pyrosequencing-based 16S rRNA and metagenomic data obtained from elemental sulfur deposits produced annually on the ice surface at Borup Fiord Pass in the Canadian High Arctic to define feedbacks between the geochemistry, microbial community composition, gene abundance, production of organic rich matrices and the chemical speciation of S 0 rich deposits during their rapid precipitation and long-term preservation. This presentation will integrate findings from recently papers by Gleeson et al. [1], Wright et al. [2], Grasby et al. [3], as well as data from sulfur speciation mapping and x-ray absorption spectroscopy of modern sulfur deposits and “paleo” spring systems preserved in permafrost (Lau et al., unpublished).


Habitability and Hydrogen Generation in Peridotite Aquifers

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The habitability of peridotite aquifers depends upon the rate of generation of energy sources such as H 2 and CH 4 during low-temperature water-rock interactions, as well as the availability of oxidants and nutrients required for microbial growth. Recent work by Mayhew et al. [1] suggests that olivine and pyroxene can produce substantial H 2 during water-rock interactions at ≤ 100°C through a surface-promoted mechanism where trace spinel phases such as magnetite, chromite and gahnite mediate electron transfer reactions between adsorbed Fe(II) and water. Mayhew et al. [1] also hypothesize microbial activity will be spatially localized to sites of H 2 production adjacent to spinel surfaces.

We will present this conceptual model for H 2-generation during low-temperature peridotite hydration, including synchrotron-based Fe K-edge multi-energy μXRF and μXANES mapping of altered olivine, pyroxene and San Carlos peridotite before and after H 2 generation. We will also demonstrate that Oman harzburgites, which contain abundant Cr-spinels, produce the highest concentrations of H 2 measured in low-temperature water-rock reactions. Changes in the Fe-speciation associated with experimental H 2 generation by Oman peridotite will be compared against μXRF and μXANES data for samples that have experienced hydration and carbonation at near-surface temperatures in the Oman ophiolite [2]. Altogether, we suggest that extensive hydrogen generation should proceed at temperatures as low as 30°C during modern water-rock interaction in Oman and other peridotite aquifers, giving rise to an enormous potential for subsurface microbial activity when oxidants such as CO 2 are available to sustain microbial growth and methanogenesis.

Effect of Solution Chemistry on the Kinetics of Step Growth

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Crystal growth from solution propagates through the attachment of atoms/molecules (in the classical theory) to the growing surfaces or aggregation of nano building clusters (in the non-classical approach) to each other. While the thermodynamic driving force for the growth is well-understood and can be precisely determined via the saturation level of the solution, our grasp of the effect of other solution chemistry parameters, such as ionic strength and stoichiometry, on the growth kinetics remained loose. In the classical approach, the net growth rate of mono-molecular layers (ie, step velocity $v_s$) is assumed to to determined by the difference between fluxes of species attaching to and detaching from kinks along step edges. Such treatment leads to the development of the wide used relationship of $v = \beta (a - a_e)/a_e$, which states that $v_s$ scales linearly with the solute activity $a$ relative to its equilibrium value $a_e$ (the kinetic coefficient $\beta$ characterizes the enthalpic and entropic barriers for solute incorporation, including desolvation of growth sites and solute particles). It then follows that $v_s$ should be controlled solely the solution saturation under similar T and P conditions. Yet, literature data from numerous cases argued strongly against this supposition. In this study, we conducted a series of in situ AFM experiments to interrogate the effect of solution chemistry parameters other than supersaturation on step kinetics using calcite as a model system. We found step kinetics were strongly affected by solution pH, ionic strength SI, and the [Ca$^{2+}$/CO$_3^{2-}$] ratio, and the impact differs in different directions (obtuse vs. acute steps on the \{104\} cleavage faces). For example, while the $v_s$ of acute steps decreased with increasing pH, the obtuse step rate showed little response to pH change. More interestingly, both sides exhibited a sharp trend transition (varied degree of positive $v_s$ – pH dependence) starting at pH ~9.5. In addition, step velocity in both directions decreased with increasing SI, but the trend became significantly weakened in the acute direction when SI > 0.1. The effect of cation-anion ratio on step kinetic appeared to be more complex. A maximum speed was achieved at different values of [Ca$^{2+}$]/[CO$_3^{2-}$] for obtuse and acute steps, and the ratio seemed to decrease with increasing pH. These observations strongly suggest that, although supersaturation, solution chemistry plays critical roles in controlling the actual growth rate and needs to be taken into consideration in kinetic studies of crystallization.

Are molybdenum concentrations and isotopes a tracer for anthropogenic pollution in the atmosphere?

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The trace metal molybdenum (Mo) is not very abundant in the environment but has found numerous applications in anthropogenic activities. For instance, in the form of Mo sulphide (MoS$_2$) it is a component of diesel fuel. Mo is used as a catalyst in many engines and is believed to be the most efficient catalyst for the hydrocracking of bitumen [1]. Molybdenum has even been suggested as a fertilizer additive [2] and has also been found in coal-fired power plant emissions [3]. Hence, anthropogenic activities may release Mo in larger amounts to the environment that may affect terrestrial and aquatic ecosystems (e.g. via its coupling with the N cycle). We have therefore investigated the potential of Mo concentration and isotope ratio measurements as a tracer of anthropogenic emissions. We measured the molybdenum (Mo) isotopic composition of aerosols collected on Teflon air filters [4]. Airborne Mo was collected at selected locations including a residence in the city of Calgary, Canada, the isotope laboratory at the University of Calgary, the University of Calgary weather station, and the City of Calgary Transit bus garage where the city buses start and idle for extended periods. Concentrations ranged from 0.07 ng/m$^3$ in the laboratory to 19.0 ng/m$^3$ in the bus garage. The $\delta^{98/95}$Mo values measured for the different urban sampling sites (reported relative to SRM 3134) ranged from ~0.18 to +0.94 •. The results of this investigation suggest that measurements of Mo concentrations and isotopic compositions have the potential to trace anthropogenic emissions in an urban environment.

Controls on dissolved REE and HFSE in glacial meltwater rivers in southern Iceland

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The chemical composition of river waters in southern Iceland is strongly affected by geological events such as volcanic eruptions (e.g., the Eyjafjallajökull in 2010), due to the input of nanoparticles and colloids from volcanic ashes.

In this study, water samples from twelve rivers and volcanic ashes were sampled twice in 2010, and once in 2011 and 2012 to characterize the geochemistry of glacial meltwaters and to investigate the impact of colloids and nanoparticles from volcanic ashes on their chemistry. The REE and other HFSE (e.g., Th, Zr, Nb and Hf) are characterized by low solubilities and high particle-reactivities. In oxic natural waters, therefore, they are not truly dissolved, but typically associated with particulates. In 0.45 µm-filtered water samples they are often well-below the lower limit of determination by analytical techniques such as ICPMS. Comparison of the trace element distribution of river particulates (i.e., filter residues) and volcanic ash to that of the respective 0.45µm-filtered glacial meltwater (i.e., sum of truly-dissolved trace elements and those that are bound to colloid-/nano-sized particles <0.45 µm) reveals very close similarities.

In 2010, rivers in SW Iceland were affected by the Eyjafjallajökull eruption, while those in the SE were not. LaCN/YbCN ratios of filter residues in the SW are in a similar range as the Eyjafjallajökull ash (EJ-1: 6.16; EJ-2: 6.58 [1]). River waters, which were sampled in August 2010, show a higher variability in the LaCN/YbCN ratio and range between 1.46 and 6.96 in the SW and 1.46 and 5.94 in the SE, but the SW rivers, which were sampled 25 days after the Eyjafjallajökull eruptions, show higher LaCN/YbCN ratios between 7.17 and 9.40. In 2011, an earthquake and a subsequent minor eruption underneath the glacier of Katla volcano caused enhanced glacial flow at the Múlakvísl river, which was accompanied by high trace element concentrations. Its LaCN/YbCN ratio of 13.5 was significant higher in 2011 than in 2010 (2.64) and 2012 (8.73). Moreover, in 2011, the Zr concentration was 222 ppt, which is several orders of magnitude higher than in 2010 and in 2012.

These results strongly suggest that natural nanoparticles and colloids of a size <0.45 µm control the dissolved REE and HFSE distribution in these rivers.


An improved hot-alkaline DNA extraction method for high cell-lysis efficiency of subseafloor microbial communities

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One of the prerequisites for DNA-based microbial community analysis is the high cell-lysis efficiency –the critical issue has been long ignored or paid very little attention despite of its significance. In fact, using a commonly used DNA extraction kit, ~80% or more of microbial cells in marine sediment are still remained as the intact form (i.e., DNA-stainable cells), indicating that the large DNA fraction of microbial components are initially biased prior to the subsequent molecular analyses.

To address this technical problem, we standardized a new DNA extraction method with alkaline treatment and heating. First, we attempted to destroy all microbial cells in subseafloor sediment samples from different depths by adding 1 M NaOH at 98 °C for 20 minutes, which treatment disrupted more than 98% of the cells in the examined samples. The DNA integrity test showed, however, that such strong alkaline and heat treatment also destroyed DNA molecules into short fragments, which could not be used for PCR-based molecular analyses. Subsequently, we optimized the alkaline and temperature condition to minimize DNA fragmentation with high cell-lysis efficiency: the best condition we standardized resulted in 50-80% of cell disruption with successfully keeping enough DNA integrity for the amplification of complete 16S rRNA gene (i.e., ~1500 bp). Also, the optimized method yielded higher DNA concentrations than those extracted by a conventional kit-based approach in all tested samples. Consequently, using the newly developed hot-alkaline method, community structure analysis of the extracted DNA assessed by quantitative real-time PCR and pyrosequencing of 16S rRNA genes showed a clear difference to the result using conventional methods, suggesting the better analytical coverage of subseafloor microbial communities than those by the conventional methods.

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Sources and concentrations of Highly Siderophile Elements in VHMS deposits through time

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The seafloor hydrothermal activity is an important mechanism of metals cycling between mantle and continental crust, producing Volcanogenic Hydrothermal Massive Sulphide deposits in various tectonic settings through time.

Concentrations and sources of Highly Siderophile Elements (HSE: Ru, Rh, Pd, Os, Ir, Pt, Au) were studied in VHMS deposits from Archean to present using new and published Re-Os isotopic data and the HSE concentrations.

In general, concentrations of HSE, as normalised to C1-chondrite, are situated slightly above the mantle values, with the exception of higher Au contents; and approximately 3 orders of magnitude lower compared to magmatic sulphides.

Remarkably, the Re/(Common Os) ratio significantly increase from Archean deposits in intra-cratonic setting to the Palaeozoic VHMS deposits in island arc setting, reaching the highest values in modern sulphides from MORB setting, with simultaneous decrease in Common Os values. This observations may be related with the change in main metal sources relative to different tectonic settings through time.

Rhenium enrichment in modern VHMS deposits may be also related with higher Re contents in present day seawater, which is along with hydrothermal fluid is one of the main sources of metals in VHMS deposits. Modern seawater is characterised by high Re/Os ratio of ~730, whereas hydrothermal fluid has much lower Re/Os ratio. In general, the Re/Os ratio increases and Os contents decrease by 2 order of magnitude from the stockwork toward the seafloor sulphides, reflecting the fluid - seawater mixing. The same pattern has been observed across hydrothermal chimneys, with higher Re/Os ratio and lower Os contents toward the outer part of chimney. This pattern is confirmed by $^{187}$Os/$^{188}$Os isotopic mixing between these two end-members, as it was shown for modern and ancient VHMS systems.

Levels and distribution of traffic related metals in Israel; Pb, Zn and platinum group metals (PGM)

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Since 1993, automobile exhaust catalysts are compulsory in Israel which obviously lead to a great improvement in the emission of toxic gases to the atmosphere. However, as these convertors contain Rh, Pd and Pt, which belong to the platinum group metals (PGM), their utilization has introduced a new contamination source to the environment.

For characterizing the extent of PGM contamination in Israel, road side soils were examined in four locations adjacent to main roads. In all sites, Pt concentrations in soils were relatively low compared to published values [1] (mostly up to 20 ng/g) and could be detected only in top soils. While Rh concentrations were below limit of detection (10 ng/g), high concentrations of Rh and Pt were found in mixed soil and dust surface samples.

Road dust collected along a half km inclined road with heavy traffic yielded very high concentrations of both Pt and Rh (260 to 1480 ng/g and 80 to 440 ng/g, respectively). Remarkable difference was observed between the uphill and downhill at the same location where concentrations uphill were 4-fold higher than downhill direction for both metals, indicating significant PGM emission with increased engine activity.

Elevated trace metal concentrations of traffic related metals (Cr, Cu, Ni, Pb and Zn) were noted for the road dust samples. However, only Zn concentrations exhibit a positive correlation with Pt and Rh concentrations and display a distinct 2-fold enrichment in the uphill direction probably due to tire friction. On a plot of $^{208}$Pb/$^{206}$Pb vs. $^{206}$Pb/$^{207}$Pb along with potential Pb sources, all samples are slightly shifted from a mixing line between the known Pb IC petrol values used in Israel and natural sources. No systematic hill slope pattern was observed. The slight shift of data points from mixing suggests an additional yet undefined, anthropogenic source. Hence, while PGM metals and Zn exhibit current contamination, Pb probably represents re-suspension of dust and soil surfaces that still carry the pre-unleaded petrol signature.

Discovery of a "vital" bacterial effect in the formation of biogenic carbonates

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Carbon and oxygen stable isotope compositions of carbonates are widely used to provide information on their conditions of precipitation. However, most carbonates result from a biological activity, which in the case of some skeleton-forming eukaryotic organisms has been shown to lead to isotopic characteristics that differ from those expected for isotope equilibrium. The origin of this difference remains poorly understood and is referred to as the “vital effect”. So far, potential microbial vital effects have been overlooked and microbial carbonation is considered from an oxygen isotope perspective as occurring at equilibrium with water. We revisit this assumption by performing an isotope study of carbonates precipitation by the strain *Sporosarcina pasteurii*, a bacterial model of carbonatogen metabolisms. Its ureolytic activity produces ammonia (thus increasing the pH) and dissolved inorganic carbon (DIC) that precipitates as solid carbonates. 

$^{18}$OCaCO$_3$ results show values up to 20‰ lower than what was expected for carbonate precipitation in equilibrium with water. This demonstrates for the first time that bacteria may precipitate carbonates with a vital effect. The addition of carbonic anhydrase, an enzyme able to equilibrate the oxygen isotopes between DIC and water, yields equilibrium values. This result demonstrates that the vital effect observed in solid carbonates results from disequilibrium between DIC and water, a mechanism also strongly suspected to account for vital effects in skeleton-forming organisms.

X-Ray Spectroscopy and Spectromicroscopy Study of Sulfur Speciation in Urban Soils

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This study shows the applicability of sulfur x-ray spectroscopy and spectromicroscopy to analytical problems in urban soils.

A combination of x-ray microscopy, elemental mapping and XANES spectroscopy at the K-absorption edge of sulfur was used to analyze the elemental and particulate composition of an urban soil loaded with debris from WWII, exemplarily from Berlin, Germany. The goal was to specify and analyze the sulfur pool of soils with major anthropogenic impact, i.e. the dumping of war debris. This impact obviously influences soil composition and soil formation processes, but may, due to sulfate leaching, also be a substantial risk to urban water quality. The sulfur load of different debris components was studied and the sulfur content of different soil samples was evaluated and correlated to different parameters, such as position of the respective soil horizon within the soil profile or location of the soil profile in the surrounding terrain. With XANES spectroscopy, the averaged sulfur pool of whole soil horizons as well as of single debris components was studied. With X-ray fluorescence imaging and spectromicroscopy, soil aggregates, debris particles, and soil solution were analyzed on the micrometer and sub-micrometer scale. Different soil and debris constituents could be assigned to elemental distribution patterns within collected fluorescence maps, allowing for a detailed analysis of the sulfur pool and release from war debris in subsequent studies. These measurements show highly heterogeneous sample composition and clear gradients in sulfur speciation and oxidation state within single particles. The weathering of the anthropogenic material is therefore directly observable. A detailed understanding of this sulfur lixiviation is central to preserve urban water quality.

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Advances in Mass Independent Isotopic Studies

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Since the first discovery of a chemically produced mass independent isotopic fractionation process by Thiemens and Heidenreich in 1983 the extent of applications of MIF in nature has expanded across a extensive range of applications that encompass much of terrestrial geochemistry, cosmochemistry, atmospheric science, and climate analysis. Time scales extend from the present to the origin of the solar system, more than 4.5 billion years ago to present. The creation of the INTRAMIF program exemplifies the extent of these investigations.

In the original work on ozone formation, it was shown there is not only a mass independent fractionation that duplicated the pattern observed in meteorites in oxygen and consequently has application in solar system evolution. A major follow up to that work is determining the actual physical chemical mechanism responsible for the effect, which remains elusive to this day. The role of chemical processes in the early solar system for the source of the anomaly in the early solar system is now agreed upon as compared to nuclear processes. Very recent experimental work has deepened understanding of processes will be presented.

The process of formation of isotopically anomalous ozone in the atmosphere has been used to trace chemical and dynamically processes in the atmosphere and has been applied to most major cycles. This includes SOx, NOx, CO2, CO, N2O, water, carbonates, chlorates, and O2. The use of high sensitivity analysis of these species has been demonstrated to provide an analytical tool to decipher chemical reaction pathways which are otherwise identifiable by conventional technique as a consequence of using multiple isotope ratio measurements.

Through polar ice studies these processes have been studied through long time scales (present – Holocene). Sulfur isotope measurements have opened a new dimension in tracking the origin and evolution of oxygen in the earths earliest environment. Recent work has shown that from Mars meteorite oxygen analysis of bulk silicate, water, and secondary minerals that the processes of Mars formation and evolution is less well understood than previously believed and will be discussed.

Modeling non-equilibrium uptake of Se(IV) upon calcite precipitation

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Selenium is relevant as a nutrient or poison for animal and human life, and as long-lived radionuclide 79Se in the context of nuclear waste management. We investigated time-dependent Se uptake by growing calcite as a possible way of Se immobilization. Calcite precipitation from aqueous solutions in presence of Se(IV)O32- was studied under the surface-controlled steady state conditions at low-to-moderate supersaturation in mixed flow reactor (MFR) experiments [1]. We then simulated MFR experiments using the GEM-Selektor v.3 geochemical code [2].

Calcite precipitation rates predicted using [3] were systematically higher than the rates observed in MFR experiments in Se(IV) - containing solutions. This corroborates the inhibiting effect of aqueous Se(IV) on calcite growth reported before [4]. To account for this effect, an inhibition term involving the Se(IV)O32- ion activity was added to the rate equation [3].

Measured amounts of Se(IV) incorporated in calcite overgrowths are substantially higher than those predicted by the atomistic calculations for the solid solution- aqueous solution equilibrium [1]. This can be interpreted by invoking an extremely strong surface growth entrapment mechanism, accounted for in our unified uptake kinetics model [5]. This model was able to describe the observed concentrations of Se(IV) in calcite overgrowths by considering a very high Se surface enrichment factor (1.5·107) with a rather low sub-surface diffusivity (10-10 nm2/s). These parameters for Se(IV) oxyanion differ significantly from those typically used in modeling entrapment effects for cations (Sr, Cd, Co) in calcite [5]. Possible reasons for this difference will be discussed.


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The PSI/Nagra Chemical Thermodynamic Database 12/07: Present status and future developments

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The PSI/Nagra TDB has been updated from version 01/01 [1] to version 12/07 to support the ongoing safety assessments for a deep underground repository for radioactive waste in Switzerland. TDB 12/07 contains three types of data: (1) Core data are widely accepted data of high-quality that are mainly based on the CODATA key values. (2) Recommended data are also of high quality, but they originate from rather active fields in the environmental sciences and may be revised over time. They are mainly based on the critical reviews of data for U, Am, Tc, Np, Pu, Ni, Se, Zr, and Th provided by NEA in their "Chemical Thermodynamics" series. (3) Supplemental data are suitable for scoping calculations. Some estimates are made in cases where their omission would lead to obviously erroneous results. TDB 12/07 is provided for use with the geochemical modeling codes GEMS [2] and PHREEQC [3].

Further development of the database will run along the following lines: (1) Data for Sn will be included from the latest NEA review [4] and for Fe and Mo from forthcoming NEA reviews, as well as data from the IUPAC reports, e.g. [5], on the chemical speciation of environmentally significant metals (at present Hg, Cu, Pb, and Cd). (2) Since a large part of the data included in TDB 12/07 is applicable only at 25°C, estimation methods [6] have to be considered for extending the application range to the higher temperatures expected in the repository environment. (3) Experimental data were reduced to zero ionic strength by NEA and IUPAC using the specific ion interaction theory SIT [6]. SIT coefficients are not known for many aqueous species (especially in NaCl background media). In order to use the SIT in geochemical modeling of natural systems, estimation methods have to be found to fill these gaps.


Biogeochemical cycling of nitrogen on the early Earth

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There has been considerable recent interest in variations of the nitrogen isotope composition of ancient organic matter and associated sediments as they provide clues for the early evolution of Earth’s atmosphere-ocean-biosphere system. In particular, large δ15N isotopic variations recorded from the Mesoarchean to the Paleoproterozoic have been linked to the evolution of the biogeochemical cycle of nitrogen toward its modern —microbially mediated— web of reactions. The biogeochemistry of nitrogen is strongly dependent upon oxidation-reduction reactions, and thus secular variations in δ15N most probably underline the protracted oxygenation of Earth’s oceans and atmosphere, during a period of roughly 700 Ma between 2.7 and 2.0 Ga.

This contribution provides a synthesis of observations made so far from Archean to Mesoproterozoic sedimentary environments. We present an extensive δ15N database: 874 published δ15N values measured on various sedimentary lithologies and phases, including kerogen, phyllosilicates, shales, carbonates, cherts, Banded Iron Formations and N2-bearing fluid inclusions. The compilation spans from 3.8 Ga to 1.4 Ga and we use statistical methods (Gaussian Kernel functions) applied to geochemical times series for its analysis.

Accordingly, we suggest that the anaerobic process of nitrogen fixation and ammonium assimilation evolved early in biological evolution during the Paleoproterozoic or earlier. Mesoarchean 15N enrichment of +15‰ in average and up to +50‰ most probably record the initiation of the oxidative part of the nitrogen cycle including nitrification and denitrification. A second positive nitrogen isotope excursion is recorded during the Paleoproterozoic at around 2.0 Ga and might reflect the fluctuation of a redox transition zone where NH4+ would be present in the deep anoxic ocean and NO2- and NO3 would accumulate above the oxic-anoxic interface in response to increasing atmospheric and oceanic oxygen concentrations. A complete nitrogen biogeochemical cycle including its oxidative part might thus be recorded since the Paleoproterozoic, in line with the view that free oxygen had stabilized NO3 in the surface oceans by that time. Increasing number of δ15N measurements through the Precambrian rocks record would help to refine these interpretations.

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An experimental investigation of the formation mechanisms of superdeep diamonds
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The subduction of oceanic crust is not only a fundamental driving force of mantle convection, but also an integral part of the Earth’s deep carbon cycle. Subducted material provides almost all of the return flow of carbon to the earth’s interior [1]. Seismic tomography suggests that slabs can penetrate into the deep mantle, thus carbon can potentially be delivered into the transition zone and/or lower mantle and react with ambient mantle [2].

Recent studies of superdeep diamonds from the Collier-4 [3] and Juina-5 [4] kimberlite pipes in Brazil have found direct evidence for such processes. The diamonds show complex growth structures, are composed of isotopically light carbon (ranging up to -25‰) and contain mineral inclusions with compositions expected to form from a mafic protolith in the transition zone and/or lower mantle and react with ambient mantle [5].

Geochemical modelling suggests that inclusions, and their diamond hosts, crystallised from a low degree carbonated melt of subducted basalt in the transition zone upon reaction with ambient mantle [5].

This study aims to test the model of superdeep diamond growth by experimentally investigating the liquidus phase relations and reactions that occur when an oxidized carbonated melt interacts with reducing mantle peridotite. The bulk composition used to determine the appropriate melt composition represents ODP hole 1256D basalt samples containing 2.5wt% CO₂. Initial multi-anvil experiments at 20 GPa show that two immiscible melts, a Na-rich carbonate melt (~16wt% Na₂O) and a Na-bearing ‘granite’ melt (>70wt% SiO₂) coexist with majorite at 1400-1500°C. We will report on ongoing experiments in which these melt compositions are reacted with reducing peridotite.


Bacterial communities inside soil iron nodules
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Iron nodules are found in a wide variety of surficial environments across the globe [1, 2] and iron spherules of a similar size and morphology are even found within the sediments of Mars [3].

Iron nodules from soils in Western Australia are homogenous, compound and concentric and dominated by hematite and maghemite. Nodule formation has been attributed to weathering and the mobilisation and migration of Fe²⁺ in response to variations in redox potential and differential drying [1].

Bacterial communities within the soil nodules were investigated using cloning and sequencing of polymerase chain reaction amplified 16S rRNA genes. The results showed that the nodules contain a phylogenetically diverse bacterial community dominated by members of Acidobacteria, Actinobacteria and Proteobacteria.

The metabolic potential of uncultivated organisms within the soil nodules can be phylogenetically assessed by a comparison with related sequences from environmental clones or cultured bacteria. The results show that some clone sequences closely resemble cultured Fe-oxidising bacteria and clones from environments with high concentrations of iron. The combination of geochemical and bacterial studies can provide new insights into nodule formation and the role bacteria play in the mineralisation process.

Reactive transport modeling of carbon, chlorine, and hydrogen CSIA data to improve monitored natural attenuation for chlorinated ethenes

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Compound-specific stable isotope analysis (CSIA) has been shown to provide an improved insight into the monitored natural attenuation (MNA) of chlorinated solvents. The work presented here focuses on the simulation of carbon (C), hydrogen (H), and chlorine (Cl) isotopes of chlorinated ethenes with a reactive transport model (RTM) calibrated by CSIA data. Such a model allows for the simulation of variations in concentrations and isotope ratios in aquifer systems as result of various degradation pathways and transport processes. The base RTM model was calibrated for C, H, and Cl isotope fractionation observed during complete reductive dechlorination of TCE in a microcosm experiment. Secondly, the Operational Unit 10 at the Hill Air Force Base site (Utah, USA) was intensively sampled. This intricate site presents two plumes of chlorinated solvents (PCE and TCE), which partly mix. Moreover, based on earlier MNA studies, both reductive dechlorination and aerobic oxidation are likely to occur as the aquifer conditions range from oxic to anoxic.

Results/Lessons learned

We present (i) the model background, which includes the highlights provided by the microcosm experiment, discuss (ii) the collection of CSIA data at the complex field site, and illustrate (iii) potential applications of the model, notably for the interpretation of the above-mentioned field data. The use of CSIA data at the field site reveals the complexity of the studied aquifer, where degradation is shown to mostly occur in restricted areas.

Relevance of mass transfer processes for the interpretation of stable isotope fractionation

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In recent years, compound specific stable isotope analysis (CSIA) has become an established tool for assessing (bio)degradation of organic contaminants within aquifers. The fractionation of stable isotopes during degradation leads to observable shifts in stable isotope ratios which can serve as a qualitative indicator for in situ contaminant degradation. However, to use stable isotope data to obtain quantitative information on in situ biodegradation requires among others knowledge on the influence of mass transfer processes on the observed stable isotope fractionation.

Mass transfer processes in aquifers range from macroscopic transport including dispersion driven mixing processes to microscopic transport processes controlling the microbial availability of the contaminant. These transfer processes may cause itself an additional fractionation of stable isotopes, but even in the absence of such additional fractionation the mass transfer processes need to be considered for a quantitative analysis of stable isotope signatures [1,2].

This presentation will introduce theoretical and reactive transport modeling concepts on combining mass transfer processes into a quantitative analysis of stable isotope fractionation and the determination of degradation pathways using stable isotope signatures of two different elements. Examples for the verification and application of these concepts will be presented showing the relevance of mass transfer processes at different scales for the interpretation of stable isotope fractionation.

Lithium and oxygen isotope compositions of basaltic glasses from ridge axes and off-axis seamounts in the northern EPR (10-15°N)

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Geochemical variations in mid-ocean ridge basalts (MORB) have been attributed to the presence of compositionally distinct mantle components in their source, which may include subduction zone processed oceanic sediment, crust and upper mantle material. The light stable isotopes of lithium and oxygen could be potential tracers of compositionally distinct mantle components in their source, alteration and subduction processes. We present a study of lithium and oxygen isotopes on a group of well-characterized basaltic glasses from both ridge axes and off-axis seamounts in the northern East Pacific Rise (EPR) between 10°N and 15°N. The samples range from normal-MORB to enriched-MORB in composition.

Our results show that the δ7Li values of these glasses vary from 3.1 to 5.2‰, which systematically correlate with other geochemical indices of mantle heterogeneity, forming trends toward a more enriched composition. In detail, heavier Li isotopic ratios are associated with higher highly/moderately incompatible element ratios (e.g., K2O/TiO2 and Ba/Y), more radiogenic 87Sr/86Sr and less radiogenic 143Nd/144Nd. On the other hand, the oxygen isotope compositions display a fairly narrow range of 5.44 to 5.68‰ (equal or lower than upper mantle whole rock values), do not correlate with other geochemical indices and, thus, could not provide clear information on the nature of mantle heterogeneity. Previous studies have shown that lateral compositional variability exists in the upper mantle beneath the EPR; this lateral compositional variability is reflected by the lithium isotope variability of axial and off-axis seamount volcanism. Moreover, lithium isotopic data seem to record the incorporation of a heavy-Li-enriched component, most likely a recycled subduction-metasomatized mantle [1], into the suboceanic mantle in the eastern Pacific.


Enriched mantle source and petrogenesis of the Miocene ultrapotassic rocks in western Lhasa block, Tibetan Plateau: Lithium isotopic constraints

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The authors have successfully applied lithium isotope to the typical study of Sailipu, Dangreyongcuo, Xurucuo and Chazi ultrapotassic rocks in southwestern Tibetan Plateau. Lithium concentrations of 33 whole-rock samples show a range from 11.2 ppm to 46.1 ppm. Lithium isotopic compositions exhibit a variable range of δ7Li values (-3.9 to +3.5 ‰) with an average δ7Li of 0.1 ‰ that corresponds to the average of upper continental crust (Teng et al., 2004). Lithium isotopic compositions of UK from SW Tibet do not show any significant correlations with the degree of magmatic differentiation, as inferred from various compositional parameters (e.g., SiO2, Li, Rb and Ga). This suggests insignificant Li isotope fractionation during ultrapotassic rock differentiation, reflecting the source characteristics (Teng et al., 2009). Lithium isotopic compositions of these samples vary by 7.4 ‰ and do not correlate with radiogenic isotopic compositions or chemical and mineralogical parameters. The Li isotopic heterogeneity therefore likely reflects heterogeneous source rocks (Teng et al., 2009). Based on calculation modeling and a comparison with the previous similar results (Agostini et al., 2008; Janousek et al., 2009), the authors hold that the most probable metasomatic agents were melts or fluids derived from subducted Indian crust instead of from Tethyan crust (including sediments). Therefore, the authors put forward a petrogenetic model of ultrapotassic rocks in southwestern Tibetan Plateau.

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On the evolution of the Western Alpine Orogen: U-Pb geochronology and Hf isotopic ratios in zircons from Adamello and Bergell amphib-rich mafic and ultramafic rocks

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The orogenic belt intrusive rocks are mostly silica-rich products in which the shallow-depth crustal contamination commonly obscures the original mantle geochemical signal. The rare mafic and ultramafic rocks associated with the major intrusive bodies represent a fundamental petrological tool to track back the evolution of the orogen. The reconstruction of the Cenozoic paleogeography and the tectonic evolution of the Western Alps is still matter of debate, with complex geological models involving multiple oceans (i.e., Ligurian-Piedmontese and Valais oceans) incorporating micro-continents (i.e., Briançonnais domain). Also the origin of the Periadriatic magmatism, developed from ~44 to ~31 Ma along the Alpine belt, and its relationship with tectonic evolution of the Alpine Orogeny remains partly unclear.

We carried out U-Pb geochronology and Hf isotopic ratios on zircons from amphibole-rich mafic and ultramafic rocks of the Adamello batholith and the Bergell pluton, the two largest Cenozoic intrusive bodies of the Alpine Orogen. Results show that the Bergell mafic rocks formed ~10 Ma later than the Adamello analogues. In addition, the Bergell gabbros have a more enriched Hf isotopic signature than the Adamello counterparts. We propose that the formation of the oldest mafic rocks from the Adamello batholith is related to the subduction of the Ligurian-Piedmontese oceanic lithosphere. The mafic rocks from the Bergell pluton most likely record the partial recycling in the source of the continental material. These rocks are presumably related to the younger subduction of the Valais basin, which followed that of the Briançonnais continental block.

Abrupt shifts in Horn of Africa hydroclimate since the Last Glacial Maximum

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The timing and abruptness with which Africa transitioned into and out of the Early Holocene African Humid Period is a subject of ongoing debate, with direct consequences for our understanding of African climate stability, paleoenvironments, and early human cultural development. Here we present a new proxy record of hydroclimate, based on the hydrogen isotopic composition of leaf waxes, from a marine core in the Gulf of Aden that documents rapid, century-scale transitions into and out of the African Humid Period across the Horn of Africa. Similar and generally synchronous abrupt transitions at other East African sites suggest that rapid shifts in hydroclimate are a regionally coherent feature. In addition, the termination of the African Humid Period in East Africa is synchronous with the termination in West Africa. A probabilistic analysis of the abruptness of the transitions in East Africa suggests that they likely occurred within centuries, underscoring the remarkable sensitivity of Northeast African hydroclimate to external forcings. We speculate that the non-linear behavior of hydroclimate in the Horn of Africa is related to convection thresholds in the western Indian Ocean.

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Experimental comparison of abiotic and microbial Fe-mineral transformations to identify pathways of magnetic nanoparticle production during pedogenesis

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We present results from an on-going interdisciplinary experimental study of possible pathways for producing Fe-oxide nanoparticles during pedogenesis of loess-derived soils. The phenomenon of magnetic enhancement in many soil types has been recognized for several years, but the question of whether the enhancement process is primarily driven by microbial activity or abiotic processes is still unresolved. Bioreduction experiments were carried out using the dissimilatory Fe-reducing bacteria Shewanella putrefaciens with synthetic nanoparticle preparations of Fe-oxides and oxyhydroxides including goethite, lepidocrocite, ferrihydrite and magnetite. The products of bioreduction are compared with abiotic alteration experiments to examine heating-induced dehydration and redox reactions. Bacterially-mediated re-mineralization of precursor phases produces characteristic high-purity, highly-crystalline euhedral Fe-oxides. Heating-induced dehydration of nano-goethite and lepidocrocite produces topotactic reactions which form pseudo-morphed hematite and maghemite respectively, with distinctive nanostructures containing high concentrations of crystalline defects. However, reduction-heating of dehydrated nano-goethite produces Fe-oxide with non-unique magnetic signatures and morphology that obscure the inorganic origin of the mineral product. The magnetic properties, microstructure, and morphology of the reaction products were characterized with a combination of low-temperature magnetic remanence and susceptibility, high-resolution TEM microscopy, and x-ray diffraction. This study is working toward the identification of magnetic and non-magnetic biosignatures in Fe-oxides that may help elucidate the origins of magnetic minerals in a number of environments, including soils and terrestrial sediments in addition to other planetary settings.

The nature of pyroxenite xenoliths of mantle wedge beneath the Avacha volcano (Kamchatka, Russia)

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Bulk-rock composition determined by XRF for peridotite xenoliths of Avacha volcano shows variations in petrogenic components (in wt.%): SiO2 (40.5-47), TiO2 (0.01-0.07), Cr2O3 (0.25-1.9), Al2O3 (0.3-1.8), MgO (42-48.2), FeO (7.6-10.4), MnO (0.11-0.15), NiO (0.25-0.33), CaO (0.35-1.4), Na2O (0.1-0.15), K2O (0.02-0.06). Pyroxenite xenoliths are divided into two groups: orthopyroxenites and clinopyroxenites. In comparison with the harzburgite xenoliths clinopyroxenites are characterized by lower of MgO (17-20.3), NiO (~0.02), Cr2O3 (0.12-0.3) contents and by higher SiO2 (48.6-51), TiO2 (0.2-0.45), Al2O3 (2.6-4.9), CaO (17.3-19) and Na2O (0.4-0.85) in wt.%). The bulk-rock composition of orthopyroxenite xenoliths (in wt.) is: SiO2 (49-54.8), Cr2O3 (0.3-1.2), TiO2 (0.03-0.12), Al2O3 (1.2-2.8), MgO (26.6-34.5), FeO (4.7-10) and CaO (1.4-8.5), NiO (0.08-0.15), Na2O (0.1-0.4). The chemical compositions of peridotitic and pyroxenitic minerals and their primary melt and syngenetic fluid inclusions were described in [1-2]. According to ICP-MS data primary peridotite xenoliths are extremely depleted. Metasomatized peridotite xenoliths, which contain newly formed clinopyroxene, amphibole and sometimes interstitial silicate glasses, differ from primary harzburgites by higher REE contents. Orthopyroxenites have smooth patterns with depletion in LREE ([REE/Cr]n – 2-5). Clinopyroxenites are the most enriched in trace elements compared to other ultramafic xenoliths ([REE/Cr]n – 3-0.7). Their patterns are characterized by high MREE/HREE ([Sm/Yb]n – 1.5-2.1).

Orthopyroxenites can be considered as derivatives of the metasomatized harzburgites due to their similar bulk-rock composition and features of changes in the mineral composition. Clinopyroxenite xenoliths were formed probably as a result of metasomatic transformation and melting of mantle lherzolites, but not of harzburgites of mantle wedge beneath Avacha volcano.

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Invisible gold in arc volcanic glasses


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We present new EMPA major and LA-ICPMS trace element data from submarine basaltic to rhyolitic volcanic glasses recovered from the Kermadec arc volcanic centers Monowai, Brothers, Healy, Cotton, Rumble II West, Rumble III and Clark. During time-integrated analyses, invisible nano-sized nuggets rich in Au, Ag, Mo, Sn, Sb and W—mostly located along microlite or microcrystal-glass boundaries—were identified and then mapped using LA-ICPMS. Field and experimental evidence suggest that hot gases exsolve from magmas and accumulates as bubbles, can act as a carrier for metals, including Au and Ag. Mainly due to changes in temperature, pressure, flow regime and melt characteristics (i.e., viscosity, volatile saturation, and so on) during the ascent of the magma and quenching of the lava during eruption, the bubbles become unstable and may collapse, subsequently depositing metal-rich nano-nuggets in the glass. The localised occurrence of the nano-nuggets indicates a heterogeneity in the metal-contents of the gas phases exsolved from the ascending magma. In addition, imperfections, such as microcrystals, may act as nucleation point for nano-nuggets, which can explain their common occurrence along microcrystal-glass boundaries. Furthermore, these nano-nuggets appear to preferentially occur in basaltic glasses rather than in silica-rich glasses, suggesting there is an influence of magma type on the metal-bearing capabilities of the exsolved gases (bubbles). The formation of nano-nuggets in Kermadec arc glasses most likely represents a syn-eruption metal enrichment, possibly representing an indication of the ore forming capabilities of magmatic sources.

Niobium and Tantalum Mineralization in the Nechalacho REE Deposit, NWT, Canada

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The Nechalacho Layered Nepheline-Aegirine Syenite suite at Thor Lake, North West Territories, situated within the alkaline to peralkaline Blachford Lake Complex, contains substantial reserves of Rare Earth Element (REE), zirconium, niobium, tantalum, and gallium in two ore zones (Upper and Basal zones). Pervasive hydrothermal alteration, involving replacement of primary magmatic mineral assemblages by an assemblage comprising K-feldspar, biotite, zircon and magnetite, influenced the upper 300 m of the layered suite, including the niobium-tantalum mineralization, which occurs in both ore zones. This was followed by albitionization.

Previous studies of niobium and tantalum mineralization have focused on pegmatites, in which they occur as magmatic columbite group minerals that vary compositionally due to crystal fractionation. Unlike most pegmatites, niobium and tantalum at Thor Lake are hosted mainly by secondary minerals, i.e., fergusonite-(Y) and columbite group minerals, and as minor components in zircon. In the Upper ore zone, columbite group minerals occur within the altered cores of zircon crystals and immediately surrounding these crystals. Fergusonite-(Y) displays similar textural relationships with zircon in the Basal ore zone. Primary magmatic columbite group minerals have been identified only within drill core intervals of unusually high bulk iron content.

We propose a model in which niobium and tantalum were concentrated at the magmatic stage in a zirconium-silicate, such as eudialyte in the Basal ore zone or within zircon in the Upper ore zone. The zirconium-silicate, eudialyte, was decomposed by hydrothermal fluids, resulting in the formation of zircon with yttrium-rich cores. Fergusonite-(Y) then crystallized during hydrothermal alteration of these zircon cores in the heavy REE-enriched, Basal ore zone. Simultaneously, alteration of yttrium-poor zircon in the heavy REE-depleted Upper ore zone led to the formation of fine-grained columbite group minerals. Locally, primary columbite group minerals crystallized and were later metasomatically altered within iron rich horizons of the ore zones. As opposed to other niobium and tantalum-bearing intrusions, the minerals in the Nechalacho Layered Suite that host these two metals are predominantly of secondary origin.
WHAM-$F_{\text{Tox}}$: An aquatic cation mixture toxicity model

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An important reason for the development of geochemical models of natural waters is to predict and explain toxic effects towards aquatic organisms. We have extended the WHAM chemical speciation model [1,2] for application in toxicity, by assuming that the binding sites of living organisms can be represented by those of humic acid. The calculated cation accumulation ($\gamma_i$ mol g$^{-1}$), or “active body burden”, measures the exposure of the organism, and is combined with a cation-specific toxicity coefficient ($\beta_i$) to quantify the toxic effect via the combined variable $F_{\text{Tox}}$ ($= \sum \gamma_i \beta_i$).

The toxic response is set to zero when $F_{\text{Tox}} \leq F_{\text{Tox},L}$ (lower threshold) and 100% when $F_{\text{Tox}} \geq F_{\text{Tox},U}$ (upper threshold) with a linear response in between (Figure 1).

![Figure 1: Laboratory toxicity of Cu, Zn and Cd to zebra mussel [3]; data fitted with WHAM-$F_{\text{Tox}}$.](image)

The model has been used to interpret observations of macroinvertebrate species richness in > 400 streams affected by acidification and/or abandoned metal mines [4]. This field application required the use of quantile regression to take into account variations in species numbers due to factors other than the chemical composition of the streamwaters.


Composition of COH fluids up to 2.4 GPa: A multi-method approach

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The mass transfer from the subducting lithosphere to the overlying mantle wedge is mediated by complex solutions resulting from dehydration and decarbonation processes. Compared to $\text{H}_2\text{O}$-only and $\text{CO}_2$-only fluid compositions, experiments dealing with mixed $\text{H}_2\text{O}$-$\text{CO}_2$ fluids in equilibrium with high-pressure minerals are limited. In order to investigate the speciation and the solute contents of COH fluids in equilibrium with mantle minerals we performed two sets of experiments at identical $P$, $T$ and $f_{O_2}$ conditions using a rocking piston cylinder apparatus. Synthetic forsterite with minor enstatite was used as starting material.

In the first set of experiments we investigated the composition of COH fluids by puncturing the capsule in a gastight PTFE vessel at $T=80^\circ\text{C}$. Evolved gases were convoyed toward a quadrupole mass spectrometer through a heated line to avoid the condensation of water. Oxalic acid dihydrate and graphite have been used to generate the COH fluid. Experiments were conducted at $f_{O_2}$-controlled conditions using NNO, OH (GX, COH) buffer and a double capsule technique. Following thermodynamic modeling we expect in our experiments fluids close to the binary $\text{H}_2\text{O}$-$\text{CO}_2$ join.

The second set of experiments was performed to determine the solubility of forsterite in COH fluids. We analyzed the fluid trapped in a diamond layer by the cryogenic laser-ablation inductively coupled plasma-mass spectrometry technique [1]. COH fluids were generated from the addition of graphite, anhydrous oxalic acid and water.

The results will highlight the importance of COH fluids for the mass transport in subduction zones. Comparisons with other experimental systems [2] and with thermodynamic calculations will also be shown.

The distribution of LILE and HFSE in the magmatic hydrothermal systems of the detachment-closed metamorphic block (Eastern Trans-Baikalian region, Russia)

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Among the mylonites of the Borschovochy detachment-related metamorphic block with the Early Cretaceous age, simultaneous sills of andesites and dacites are forming. Their intrusion is accompanied by a hydro-thermal change of mylonites. Three main types of metasomatic associations are defined: K (white mica + chlorite + quartz ± adularia), Na-Fe-Ca (chlorite + albite + hematite + epidote + calcite), and K-Ca (quartz + calcite + ankerite + muscovite ± chlorite).

For unchanged metasediment mylonites, the way LILE and HFSE are enriched corresponds to the UK standard with only differences in Cs (7-15 ppm) and Rh (92-135 ppm) enrichment, and low content of Sr (24-133 ppm). Geochemical characteristics of andesites and dactites show their similarity to amphibolites from the island arcs and active continental margins.

Metasomatism stimulates the loss of the most LILE and HFSE. At the same time, Ti is added to the Na-Fe-Ca system (up to 0.8 – 2%) with maintaining the Zr, Hf, Nb Ta, and REE concentrations. It is noted that maximum microelements are removed in the K- and K-Ca systems due to Sr enrichment (150-490 ppm) and inert Ti behavior (0.1 – 0.9%). It is obviously demonstrated in geochemistry of the frontal and rare zones, where Th decreases from 2.9 to 0.1 ppm, Zr - from 74 to 3, 2REE from 79 to 13, La/Yb from 6 to 1.5.

A main mechanism for the extraction of REE is assumed to be the monazite decay, which discovers reaction crown composed by xenotime and galenite when contacting with sulfides.


Introducing PT-HPLC

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High-Performance Liquid Chromatography (HPLC) systems are superior in many respects to gravity-driven open columns commonly used in geochemistry, yet they suffer from several shortcomings that have hampered their adoption in isotope geochemistry (e.g. the liquid flow path often contains glass and/or metal parts which are easily corroded/dissolved, electronic controls and housing are often spatially associated with the HPLC unit, shortening the system lifespan [e.g. 1]).

Here, we present a system developed at the Origins Lab. which addresses many of the shortcomings of commercially available HPLC systems: Pneumatic Teflon-HPLC (PT-HPLC) [2-4]. Development of this system was aided by technological transfers from the semi-conductor industry and the availability of Teflon-manufactured parts. Its key features are:

1) fully automated elution schemes controlled through LabVIEW software interface, which enables for (i) fresh mixing of reagents for each elution step and (ii) gradient/ramp elutions, while removing the human error/non-reproducibility component, 2) temperature control of the system (up to 80°C) for enhanced chemical separations [5], 3) a modular design making the system adaptable to a variety of separation schemes by quick and inexpensive change of the resin type or column length, and 4) pneumatic actuation, allowing for the electronics to be isolated from the HPLC unit, increasing the lifespan of the system.

To test the PT-HPLC we performed a separation of all REE from each other in one column pass with unprecedented resolution. We used a 70 cm long column (ø=0.3 cm) filled with Ln-resin (25-50 µm bead size), a constant temperature of 70 °C, a flow rate of ~0.5 mL/min and a HCl molarity ramp slowly increasing along a convex path from 0.10 M to 10 M HCl. More than 99% of each multi-isotopic REE was separated from its neighbors in one column pass.

This result demonstrates the effectiveness of our system and its great potential to tackle all outstanding geochemical problems that call for demanding separation schemes [6].

The role of pH and simple organic molecules in amorphous calcium carbonate (ACC) structure

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CaCO₃ crystallization controls a large part of the global carbon cycle through fluid-rock interactions, the formation of biominerals and also industrial processes. The initial steps of CaCO₃ crystallization are known to occur via the formation of amorphous calcium carbonate (ACC). The stability of ACC and its crystallization kinetics have been shown to be affected by temperature, pH and (in)organic additives [1]. However, little is known about the effect of these parameters on the structure of ACC at the atomic scale. Obtaining this information would help explain the different stabilities, morphologies, surface properties and formation mechanisms of CaCO₃ biominerals.

We carried out atomic pair distribution function (PDF) analysis using synchrotron radiation to determine the ACC structure formed under various conditions of pH and organic compounds. The results were combined with data from X-ray photoelectron spectroscopy, powder X-ray diffraction, infrared spectroscopy (FTIR) and electron microscopy.

PDF results showed that the short range ordering for ACC (<15 Å) was notably affected by increasing the initial pH of the Na₂CO₃ solution from 10 to 14 (figure left). This difference could indicate an association of the hydroxyl ions with ACC at higher pH, possibly affecting the water content. Conversely, ACC structure remains virtually unaffected when it forms in the presence of several organic compounds (e.g., amino acids, polysaccharides). FTIR revealed small changes in the mode of vibration of carbonate bands and also in water content for certain organic compounds (e.g. citric acid) indicating considerable surface interaction between the organic material and ACC.


Spatial distribution of heavy metals in the urban soils of Chisinau city (Republic of Moldova)

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The study area comprised the entire area of Chisinau city and has an approximate dimension of 15/15 km². Soil samples were collected inside the network of 1km/1km², from the depth 0-20 cm. On the grid surface, 120 soil samples have been analyzed. The heavy metal content was analyzed using X-ray Fluorescence Spectrometry (EDXRF Epsilon 5). The analyses for physicochemical parameters were carried out with the following methods: particle size distribution (Kachinsky, 1958), organic matter content (Tiurin, 1965), CaCO₃ (Arinuskina, 1970) and the pH was determined using a Corning M-555 pH/Ion Meter. Assessment of anthropogenic contribution in urban soils has been determinate by means of enrichment factor (EF), geoaccumulation index (Igeo) and pollution index (PI) [1].

Correlation matrix for analyzed heavy metals and physicochemical parameters was performed to observe relationship between the analyzed parameters. Results presented the chemical association of heavy metals in the study area. The physicochemical proprieties of urban soils showed a significant positive correlation with each other and with Co, Ni and Cr whose origin is predominantly geogenic. The conclusions highlighted the organic matter has an influence an accumulation of heavy metals. As well is evident that the elements showed a good correlation with each other indicating a common source. The geochemical background range at urban scale has been defined by applying the iterative 20 technique method. The background geometric mean values for heavy metals (mg/kg) are: Cr (64.2); Co (12.9); Ni (32.7); Cu (28.4); Zn (82.7); Pb (22.8) and As (9.4). The means concentration of analysed chemical elements in Republic of Moldova rocks are Cr (86 mg/kg); Co (11 mg/kg); Ni (38 mg/kg); Cu (22 mg/kg); Zn (83 mg/kg); Pb (17 mg/kg) and As (1.7 mg/kg) [2].

The calculated EF and Igeo results revealed the following order As > Pb > Zn > Cu > Ni > Cr > Co. The PI recorded content from heavily contaminated to uncominated in follwing order Zn > As > Cu > Pb > Co > Ni > Cr.

Fingerprint of last glaciation on $^2$H and $^{18}$O in groundwater of north-east part of Baltic Artesian Basin

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In the northern part of Baltic Artesian Basin (BAB) a groundwater of the multilayered hydrogeological system (mainly the Cambrian and Vendian aquifers) is the principal and most plentiful source for the public water supply in Russia and Estonia. But there are problems with the water quality in many sites due to high salinity and/or the specific components abundance. For example, the natural origin radionuclides (mainly Ra and Rn) and microelements (B, F, Fe, Mn etc.) exceed the sanitary limits.

The BAB is characterized by the limited knowledge about the hydraulic boundaries conductivities of aquifers. Taking into account the complex geological history of the Baltic region in the Pleistocene and Holocene, the isotope archive is significant for the groundwater flow and mass-transport understanding.

The stable isotopes ($^2$H and $^{18}$O) were studied in the aquifers near north-east margin of BAB from a crystalline basement to Earth surface. The fingerprint of the Baltic ice lake is clearly fixed for Cambrian aquifer in Tallinn (Estonia). The lightest stable isotope composition of groundwater for Europe was found here ($^2$H=-160 ‰, $^{18}$O=-21 ‰, Raidla et al., 2009). The isotope composition of water is gradually weighted to the east direction and make up $^2$H=-125 ‰, $^{18}$O=-17 ‰ near the boundary between Estonia and Russia, and $^2$H=-100 ‰, $^{18}$O=-13 ‰ (that is like to modern precipitation) near the Ladoga lake. It seems, a relicts of the Eemian sea water also was obtained in some cases. It is the salty (M=4-6 g/l) and isotopically fractionated water, which have no $^{14}$C or have significant $^{14}$C age. Isotope composition is weighting, if the water is the thawed permafrost and become lighter, if it is the residual water after sediment freezing.

Clarification of As(V) Sorption Mechanism with ferrihydrite for Quantitative Modelling of Coprecipitation Process in Wastewater Treatment

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Coprecipitation method using ferrihydrite has been commonly applied to remove As(V) in wastewater such as acid mine drainage. Objective of this study is to clarify how coprecipitation of As(V) with ferrihydrite occurs in wastewater and quantitative modelling of them.

We investigated the sorption mechanism of dilute As(V) with ferrihydrite using three kinds of experimental studies for an artificial wastewater in which the ion strength was 0.05 and pH was 5 and 7; (i) sorption isotherm formation, (ii) zeta potential measurement and (iii) XRD analysis. We confirmed that As(V) was formed a simple two-dimensional adsorption onto the surface of ferrihydrite when the initial As/Fe molar ratio was less than 0.4, whereas a surface precipitation of amorphous ferric arsenate was formed when the initial As/Fe molar ratio was more than 0.4 [1].

Furthermore, both of XANES and EXAFS analysis on K-edge of As showed As(V) coprecipitates with ferrihydrite was mixture of As(V) adsorbed ferrihydrite and amorphous ferric arsenate. Estimated weight ratio of amorphous ferric arsenate in As(V) coprecipitates became above 0.5 when the initial molar ratio of As/Fe=0.5 was used. These results corresponded with results by XRD analysis. EXAFS analysis assuming three kinds of surface complexes for As-Fe bond showed the coordination number for 2.85 Å of As-Fe bond increased and it for 3.24 Å of As-Fe bond decreased with increasing the initial As/Fe molar ratio. All experimental data obtained in this study showed As(V) co-precipitation mechanism shifted gradually from As(V) complexation to the surface of ferrihydrite toward amorphous ferric arsenate. Therefore, we constructed surface precipitation model to evaluate quantitatively the coprecipitation process of As(V) with ferrihydrite. Good agreement between experimental and calculated values was observed.

Selenium coprecipitated with barite as a new redox indicator

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Redox potential (Eh) is an important physico-chemical factor that can affect behaviors of various ions in water. A number of previous studies have suggested that Eh was estimated by the solid-water distribution of redox-sensitive elements based on the effect of change of the oxidation state such as relative enrichment-depletion profiles of particular elements such as iron and manganese. However, the estimation of redox conditions based on these profiles may not be reliable because (i) elemental concentrations are influenced by many factors such as secondary adsorption-desorption reactions and diageneis and (ii) only the relative evaluation of the redox condition is possible by the depth profile of particular elements. Thus, the aim of this study is to propose a new redox indicator using the oxidation states of redox sensitive element itself in a certain mineral to estimate directly the particular redox condition at the time of the mineral formation. Here, we examined incorporation behavior of selenium (Se) species to barite as a redox indicator for oxic-suboxic condition.

Coprecipitation experiments of Se with barite coupled with determination of Se oxidation state both in barite and water phases were conducted to investigate the influence of the oxidation state on the coprecipitation of Se into barite. The oxidation state of Se in water and barite were determined with HPLC-ICP-MS and X-ray absorption near-edge structure (XANES) at Se K-edge, respectively.

It was found that the Se(VI)/Se(IV) ratio in barite reflects the Se(VI)/Se(IV) ratio in water, which suggests that the oxidation state of Se in barite can work as a redox indicator showing the redox condition at the time of barite formation. Selenium(IV) is incorporated into barite under suboxic condition below the redox boundary of Se(VI)/Se(IV). Selenium(VI), on the other hand, is incorporated under oxic condition above the redox boundary of Se(VI)/Se(IV). Based on the distribution behavior of Se to barite, we conclude that the Se(VI)/Se(IV) ratio in barite can be used as a redox indicator whether barite was precipitated below or above the redox boundary of Se(VI)/Se(IV), the Eh region of which is different from the Fe(II)/Fe(III) and Mn(IV)/Mn(II) boundaries often employed as a signature of redox condition.

Insights into mantle processes from water and trace elements in olivine

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Olivine continues to be neglected in most trace element studies of mantle rocks. This is in spite of the ability of modern analytical techniques to measure accurately and precisely a diverse and petrologically useful suite of elements and a burgeoning experimental interpretative framework of partition and diffusion coefficients.

We present the results of a detailed study of water and trace elements in olivine as evidence of their utility. Samples chosen for this study are harzburgite xenoliths dredged from volcanic cones close to Ritter Island in the West Bismarck Arc, Papua New Guinea. From textural observations, these samples are assigned to ‘residual’ or ‘reacted’ groups. ‘Residual’ samples display textures indicating an origin through melt extraction and sub-solidus cooling. Olivines have very low concentrations of all incompatible trace elements and water, consistent with the nominally cpx-free mineralogy. Concentrations of Al (0.5-9.1 ppm), Cr (5.0-19.9 ppm) and V (0.09-0.63 ppm) are exceptionally low due to the exsolution of Cr-spinel plates during cooling to temperatures of ~600 °C.

‘Reacted’ samples display textures consistent with melt-rock reaction. Olivines reflect this in significant water and trace element enrichment and disequilibrium, with over an order of magnitude variation in Y (0.08-23.8 ppb), Ca (22.3-793.0 ppm), Na (0.6-22.8 ppm) and Cr (7.2-252.4 ppm) concentrations among crystals in individual samples on a sub-cm scale. These concentrations overlap with and diverge from those measured in ‘residual’ olivines.

We interpret this as re-equilibration of olivine during percolation of hydrous mantle-derived melts. The extreme trace element disequilibrium requires that this reaction occurred on a very rapid timescale, shortly before magmatic entainment. Olivine is the only phase that records this late-stage chemical exchange, due to its high modal abundance and more rapid rates of trace element diffusion. Similar studies on olivine from mantle and magmatic rocks can shed new light on the mechanisms and timescales of melt-rock reaction, transport, differentiation and magma mingling.

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Two Noble Families display what happened in their early days

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At the first glance there is nothing similar in behaviour of the refractory highly siderophile noble metals (NM) and the highly volatile inert noble gases (NG). However, all these species are extremely under abundant in the Earth’s mantle relative to the solar composition, and this common feature allows them to record processes invisible by other chemical / isotopic systematics.

Since long a post-giant-impact late veneer of chondrite-like material (LV) is widely discussed as a plausible explanation of NM elemental and isotopic abundances in the mantle [1, 2, 3]. Less attention has been attracted to the possibility that this same LV could have delivered to the Earth a volatile-rich material, characterised by, e.g., (almost) solar isotope compositions of He and Ne. Moreover, an enhanced density of this material could also stabilize a noble-species-bearing reservoir (DDP [4]), preventing its intense mixing within the convective mantle.

Chemical transport modeling shows that flux of LV materials from DDP into the mantle could be responsible for chondrite-like relative abundances of NM, solar-like light NG, and contribution of early generated radiogenic Xe isotopes [5].

New results of modeling are presented and discussed.


Platinum deposits in hardrock of the Konder massif

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The problem of finding of promising ore areas in the bedrock of Ural-Alaska type intrusion, which until recently were considered only as source of placer, is now actual. It is necessary to study the regularities of location of platinum mineralization and to find the new search criteria. Alkaline-ultramafic massif Conder (Aldan Shield, Siberia) is now a major source of mined platinum placers. The rocks, that contain the platinum mineralization, were known until now only in chromitite [1]. Chromite schlieren really are most enriched with platinum (Pt-Fe alloys) and other minerals of platinum group elements (PGM), the content of which is about 0.5 kg/t. Our research has shown the possibility of finding of platinumiferous zones unrelated to the chromite ores. Dunites with a rare accessory of chromite also contain platinum grains, ranging in size from 80-120 µm in fine-grained dunites and up to 1 mm – in pegmatoid dunites.

In addition, intensive platinum mineralization was found in the rocks area near a tectonic contact between dunite and clinopyroxenite in the eastern part of the Konder massif. PGMs occur in dunites as well as in clinopyroxenites. A significant part of the Pt-Fe grains are porous. Cooperite amount to about 30% of PGM grains. Iridium, osmium, irarsite, hollingworthite, erlichmanite, laurite, braggite, bowite, kashinite, ferromahosite, nickel-rich equivalent of cuproridisite and Pt-Pb-S unnamed phase were found in Pt-Fe alloys as inclusions. Pt-Fe alloys are sometimes partially replaced by tulameenite and Pt-Cu alloys.

Thus, chromite ore is not the only determining criterion in the search for platinum ores. Localization of platinum ore at the contact of dunite and pyroxenite, the presence of numerous sulphide and sulfoarsenidov of PGE, associated with platinum, as well as post-magmatic transformations and replacement of primary Pt-Fe alloys – all indicate the active involvement of S-, As-containing fluids in the formation of these deposits. Such conditions can be created within the permeable dunite, enabling for the migration of fluids- and PGE-rich residual melt and crystallization the platinum ore near the contact with a less permeable pyroxenites.


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Hydrogen isotopic composition of Earth’s early ocean estimated from Archean MORB in Barberton Greenstone Belt

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Origin and evolution of Earth’s seawater are still poorly understood. Hydrogen isotopic composition is a key to constrain secular change of seawater volume through time. In Barberton Greenstone Belt, South Africa, the past fragment of Archean oceanic crust is well preserved. We have systematically analyzed hydrogen and oxygen isotopic compositions of sub-greenschist facies pillow basalts in upper part of the Hoogenoeg Complex. Based on petrographic observation together with XRD analysis, almost hydrous mineral in the samples are composed mainly of chlorite with minor amounts of epidote and actinolite. Temperature dependence of isotopic fractionation factor between chlorite and water is weak both for hydrogen and oxygen, thus useful to estimate the dD values of co-existing water. The studied basalt show positive correlation between hydrogen isotopic composition and water content. This relationship is similar to those observed in typical modern basalts hydrated at the seafloor, but systematically offsets to low dD values compared to the modern example. Based on these relationship, we have concluded that the 3.5 Ga seawater and possibly mantle were both depleted in deuterium relative to modern seawater by 24±5‰. These results may suggest that Earth’s seawater would have been decreased through time due to hydrogen escape rather than increase by degassing of water from mantle imbalanced against subduction.

Tephra from Ischia: dating eruptions and geochemical changes

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Ischia is an active resurgent caldera. Volcanic activity at Ischia began prior to 150 ka, with the largest eruption being the 55 ka, caldera-forming Monte Epomeo Green Tuff (MEGT). Unravelling eruptive history from proximal deposits can be problematic due to burial, resurgent uplift and erosion. In such cases, distal tephra archives can provide valuable information about eruptive frequencies and about the long-term evolution of the volcanic-magmatic system.

Lago Grande di Monticchio (LGdM) lies 140 km east of Ischia. This annually laminated archive contains 64 Ischia tephra layers spanning 132 to 3 ka. These distal layers indicate that Ischia has experienced approximately one eruption every ca. 2100 years. We present major and trace element data for 20 of the layers and correlate 6 of these with glass data for proximal deposits.

Tephra compositions from the pre-MEGT (>55 ka: UMSA to Porticello) period comprise three compositional groups that occur repeatedly in successive eruptions. Tephra from smaller eruptions, e.g. UMSA and Porticello contain just one group, while larger eruptions, e.g. Tisichiello and Olummo record all three compositional groups. Proximal-distal correlations with LGdM indicate these eruptions span the 44 kyrs prior to the MEGT event.

Proximal-distal correlations indicate that the Schiappone eruption occurred 4.5 ka after MEGT. Post-MEGT tephra (<55 ka) record a step to lower FeO and TiO2 and form compositional groups that overlap with the pre-MEGT but are displaced to lower incompatible element contents.

MEGT tephra spans a wide compositional range, broadly overlapping the three pre-MEGT compositional groups but displaced to higher Nd and Y and containing an additional less evolved glass population. Confirmed distal equivalents of the MEGT include LGdM TM-19, Ionian Sea Y-7, and PRAD 1870 from the Adriatic Sea and probably C-18 in the Tyrrenian Sea. Therefore, the MEGT was one of the most widely dispersed late Quaternary tephras to source from the Campanian region.
Microstructural development of in situ deformed and heated polycrystalline halite in dependence of silica gel

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Our research focused on the influence of silica gel on the texture development and the mechanical behaviour of predeformed polycrystalline halite. In situ experiments help further our understanding of the fundamental mechanisms of the processes taking place during texture development. With different methods both single grain orientation analyses and the texture development in the bulk were successfully obtained.

The results show the influence of silica gel (amorphous phase) either on the texture development and on the physical properties (as stress/ductility behavior) focusing not only on bulk texture but also on the changes in the single grain orientations. The polycrystalline samples doped with silica gel show an increase in the yield strength and a higher Young's modulus (stiffness). In the texture development a preservation of the starting texture is observed, which correlates well with the mechanical behavior. The amorphous phase probably protects the single grains from deformation, preventing strain accumulation by the introduction of defects and thereby preserving the grain shape.

Heterogeneity and anisotropy in the lithospheric mantle

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Despite extensive geophysical investigations and studies of xenoliths and peridotite massifs, the lithospheric mantle, in particular beneath continents, remains a 'mysterious' layer. Seismic anisotropy data point to anisotropic physical properties, and hence structures, coherent at scales of 100s km. Receiver functions, in contrast, imply in lateral and vertical heterogeneity at scales < 10km within the mantle lithosphere, but the physical origin of the reflectors are not clear. We will present constraints on the lithospheric mantle seismic properties based on the analysis of an evergrowing database of naturally deformed peridotites and review recent studies of our group on naturally deformed peridotites. These studies highlight the role of reactive percolation of melts and fluids on the evolution of the lithospheric mantle, focusing on the creation of heterogeneity and the feedbacks between melt percolation and deformation. Based on these data, we will discuss the effect of these processes on evolution of the physical properties of the mantle, in particular the rheology. For instance, analysis of naturally deformed shows that static reactive percolation may significantly change the composition, but does not erase the fabrics and hence the anisotropy of physical properties. The latter, which is inherited from the major deformation episodes that shaped the continental plates, may be preserved for very long time spans, playing a major role on the subsequent evolution of continental plates.

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Earthquake-driven noble-gas geochemistry in Lake Van (Turkey)

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Terrigenic He release and changes in the He isotope ratio in response to tectonic activity is well known [1,2,3]. However, the very local nature of the He release from the solid earth [4,5,6,7] implies that every system considered has to be addressed as a single and unique entity. Only such case-specific assessment allows to infer possible links between geochemistry and seismic events.

Lake Van (Turkey) is one of the largest terminal lakes and the largest soda lake on Earth. The lake basin is situated in a tectonically active region characterized by the presence of major faults and volcanoes and is known to accumulate mantle fluids [7,8,9]. The societal vulnerability of the area to seismic hazards was dramatically documented by the occurrence of the devastating earthquake of magnitude 7.2 close to the city of Van on Oct. 23rd 2011. This unfortunate and tragic event offers a unique opportunity to study the related emission of fluids from the solid earth. Our research in Lake Van during the last two decades [7,8,9,10] sets a solid experimental basis for understanding possible changes in the noble gas isotope composition in the water column induced by such a major earthquake.

In this work we present the noble-gas concentrations of water samples from Lake Van acquired before and after the earthquake. We compare the new data to our previous measurements and we evaluate the potential of noble gas analysis as geochemical proxy for tectonic activity.


Soil Mineralogy, Geochemistry and Trace Element Mobility in the Bitumen Environment of Ondo state, Southwestern Nigeria

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Surface and subsurface soil from the bitumen environment of Ondo state was characterized for mineralogy, geochemistry and trace element mobility. Physical, mineralogy and geochemical properties of the soil samples was obtained using standard techniques. The soil in the study area is acidic with low cation exchange capacity. The majority of trace elements reside in residue phase. Hence, trace elements are relatively low mobile. They are therefore of little or no risk to ecosystem health. Major oxides are silica, iron oxide and alumina. Quartz, feldspar and kaolinite are dominant mineral constituting more than 99%.
Biomineralization and biomimetic synthesis of magnetite nanoparticles

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Ferrimagnetic nanoparticles are used in a wide range of environmental, technical and medical applications, including their use for the transformation and degradation of metallic and organic pollutants, as constituents of magnetic fluids, and as contrast agents for magnetic resonance imaging [1]. Most applications require nanoparticles with highly specific physical properties. While magnetotactic bacteria produce magnetosomes (membrane-bound magnetite nanoparticles) with strictly controlled sizes and shapes, the regulation of these properties is typically much less successful in laboratory syntheses. By using the biomineralization process in magnetotactic bacteria as a model system, we performed a series of biomimetic synthesis experiments in order to produce magnetic particles with strictly controlled properties.

First, the possible means of control over nanoparticle shapes were explored in abiotic precipitation experiments, by varying the iron source and/or the concentrations and types of organic additives. Depending on the applied conditions, octahedral, disk-like or elongated magnetite particles formed. We also analyzed magnetosomes from the magnetotactic bacterium *Magnetospirillum gryphiswaldense* and studied the effects of growth conditions and genetic modifications on the sizes, shapes and structures of magnetosomes. Using the available information on the genetic background of magnetite biomineralization in magnetotactic bacteria [2, 3], we designed a scheme for the bio-assisted synthesis of magnetic filaments. Mutagenized flagellar filaments were produced by inserting part of the gene of the known iron-binding protein Mms6 into the genome of *Salmonella typhimurium*. The mutagenized filaments are being used as stable protein scaffolds for the templated nucleation of magnetite, with the aim of producing magnetic ‘nanotubes’ [4].


Source Controls on the Metal Contents of Mantle-Derived Magmas

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Plume-derived magmas are thought to form by melting of mantle peridotite source but recent studies have shown that ferropicrites and Hawaiian basalts have major and trace elements contents that cannot be explained by this model. Geochemical and petrological studies suggest that their compositions are best explained by melting of olivine-free pyroxenite that formed through reaction between peridotite and melts derived from recycled oceanic crust. Pyroxenite with these composition are minor but ubiquitous component in ultramafic massifs and mantle xenolith. Basal and precious metals partition into sulfides, silicates and alloys, and their concentrations provide additional constraints on the lithology of their source. To test this hypothesis, we studied the Ni, Co, Zn, V, Sc and platinum group elements (PGE) contents of tholeiitic basalts and picrites from Hawaii and ferropicrites from Russia, Canada, and Namibia and compared their compositions with those of peridotite-derived magmas. Hawaiian basalts and ferropicrites have relatively low PGE with respect to Ni and Cu, a characteristic that has been previously attributed to a stage of sulfide saturation during magma ascent or the presence of sulfide in the residue of melting of a peridotite source. However, our study shows that Hawaiian basalts and ferropicrites are enriched in Ni-Co-Cu-Zn and depleted in Pd-Pt, but undepleted in Ru-Ir. These features are inconsistent with previous models but consistent with an olivine-free pyroxene-bearing source formed from recycled oceanic crust.

Our study show that a) the base and noble metal contents of mantle pyroxenite from Beni Boussera (Morocco) is consistent with mixing of eclogite-derived melts and peridotites, and b) the metal content of Hawaiian magmas and ferropicrites can be explained by melting of a mixed peridotite-pyroxenite mantle source. These observations have strong implication on the origin of magmatic ore deposits with mineralization characterized by high Ni-Cu tenors and high Cu/Pd and Ni/Ir ratios (e.g., Voisey’s Bay, Canada; Nebo-Babel, Australia; Eagle, USA, Jinchuan, Limahe, Lengshuiqing, Baimazhai, Jinhulake and Kalatongke, China).

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Immobilization of long-lived iodine after incorporation into apatite matrice

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Iodine-129 being long-lived volatile fission product, among with cesium-135 and technitium-99, represents a challenge for the design of repository-suited matrices [1]. The present study investigates a possibility of iodine incorporation in the forms of iodide and iodate into apatite and hydrotalcite-like matrices. The matrix should meet certain requirements, i.e. being cheap, safe, easy to synthesize, stable and environmentally friendly. Optimization of coprecipitation method for synthesis of iodine containing apatite has been done. Obtained matrices will be characterized by SEM and XRD. Stability in the temperature range 100 - 700ºC is studied. Leaching experiments in MQ water and brine will be done as well as radiation damage (α-, γ-) will be studied before the conference.

The vulnerability of subsurface soil organic carbon to *in situ* warming and altered root inputs

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Subsurface soils (>30 cm) store more than half of global soil organic carbon (SOC) and the processes governing soil C turnover vary with depth. However, most SOC research has focused on surface soil and controls on subsoil dynamics are poorly understood. We are building a whole soil profile (to 1.5 m) warming experiment in an annual grassland to study the effects of warming and root inputs on SOC dynamics throughout the profile. This presentation will describe the experiment prototype and an initiative for an international consortium of replicated experiments. The soil is heated with resistance heaters inserted to heat the profile to 4 °C above ambient while maintaining the natural temperature gradient. Highly 13C-enriched *Avena fatua* grass root litter will be added within heated and unheated plots, in a factorial with addition of a DOC mixture to simulate root inputs. A comprehensive suite of measurements — instrumented *in situ* and in the laboratory— will be used to quantify the effect of warming and carbon inputs on soil C and N cycling. To improve predictive understanding and model skill, the experiment is focused on hypotheses concerning: (1) temperature sensitivity of native SOC and new (added root litter or DOC) carbon inputs with depth; (2) the effects of simulated root-input treatments with depth; and (3) interactions between warming and new C inputs. This study is one of the first to study responses of subsurface SOC to global change factors *in situ* and is designed to enhance our understanding of deep SOC stabilization mechanisms and improve predictions of the fate of soil carbon in a changing climate.

Polybaric differenciation within a clinopyroxenite body in the feeder-zone of an ocean island volcano (Fuerteventura, Canary Islands)

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It is now widely accepted that fractionation processes and magma differentiation or mixing occur during magma ascent to the surface. However, location of these processes remains a subject of controversy, as are the existence and size of shallow-level reservoirs. This question arises particularly in the case of ocean island volcanoes, which are not supported by a thick crust.

Fuerteventura allows access to the root-zone of an alkaline ocean island volcano. The PX1 pluton is a 22 Ma-old vertically layered mafic intrusion emplaced at shallow level. It consists in a heterogeneous clinopyroxenitic body intersected by dykes of various compositions, often gabbroic, and impregnated by more evolved melts. This clinopyroxenitic body does not show any vertical or horizontal layering. Contacts against the host rock are sharp without any development of a marginal facies. In some areas, the clinopyroxenite mass is modally and texturally highly heterogeneous with numerous enclaves and blobs of wehrlite, dunite and olivine-clinopyroxenite. Enclave outlines are often blurred with progressive transition to the matrix. These features are interpreted as evidence of repeated mingling episodes of crystallizing mushes. Other places are rather homogeneous with interstitial plagioclase occurrence in olivine-clinopyroxenite. Polybaric crystallization within PX1 is inferred from mineralogical assemblages, typically varying from sp-bearing dunite with high mg# (e.g. ol mg#: 82.2 - 83.2 and cpx mg#: 84.1 - 87.3) to plg-ol-clinopyroxenites or krs-clinopyroxenites with lower mg# (cpx mg#: >75.4). Moreover, whole-rock geochemistry indicate a clear differentiation trend among all clinopyroxenite lithologies. In addition cpx frequently display growth zoning with core composition of Cr-diopside evolving towards Ti-augite rims.

We suggest that the PX1 clinopyroxenite body records at least three levels of crystallization/differentiation, i.e. an upper mantle to lower crustal stage at which formed the spinel-bearing dunitic enclaves, a mid-crustal level recorded by the Cr-diopside cpx cores and a shallow-level final crystallization stage during which residual melts were extracted from the system and erupted as subaerial basaltic flows.

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Two sources of water and pre-biotic molecules in the inner solar nebula

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Using a multi-stage model of the solar nebula (SN) we derive the chemical abundances and deuterium to hydrogen (D/H) ratios for water and pre-biotic species. The model consists of three consecutive stages described as:
- a spherical quasi-stationary core surrounded by the inter-core material of the parental cloud,
- a collapsing core forming a proto-stellar source, an extending disk, and a spherical envelope, and
- an accreting two-dimensional turbulent disk with gas and dust moving at different velocities.

The collapse is simulated by a semi-analytical solution of the magneto-hydrodynamic equations based on a multi-zone mass density. In all stages the same chemical module is used (Semenov & Wiebe [1]).

Large amounts of water and the major pre-biotic molecule H$_2$CO were produced with relatively high D/H ratios in the dust phase of the first SN stage (source 1, see figure). During the collapse these dust grains flow into the inner nebula being the accretion range of rocky planets. In this range a hot corino forms as a result of the collapse. There, hot neutral gas phase reactions produce H$_2$O and H$_2$CO (source 2) along with the equivalent desorbed species but with lower D/H ratios. Thus, this ratio distinguishes molecules originating from different sources (i.e. model stages) of the nebula.


Metal fluxes at the sediment-water interface in a reservoir affected by AMD

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Water reservoirs are a main source of water supply, and knowledge of the metal fluxes at the water-sediment interface is essential to predict their ecological quality. Moreover, redox oscillations promoted by turnover events may significantly alter metal cycling, especially if the reservoir is impacted by acid mine drainage (AMD). Under controlled laboratory conditions, several sediment cores were immersed in a tank of reservoir water and subjected to alternating oxic-anoxic conditions. A detailed sequential extraction was then performed on the sediments to speciate the metals into the solid phases, the pore and tank water was systematically analyzed, and a diffusion-reaction model was calibrated using the experimental results to quantify the reaction rates and the sediment-water fluxes.

The results showed that under oxic conditions, protons, Fe, and As decreased in the tank due to schwertmannite precipitation, whereas Al, Zn, Cu, Ni, and Co increased due to Al(OH)$_3$ and sulfide dissolution. The reverse fluxes occurred during hypoxia. The model, extended to the complete year, computed that between 25% and 50% of trace metals and less than 10% of Al precipitated under hypoxic conditions re-dissolved during the oxic period, while only 22% and 9% of the Fe and As precipitated under oxic conditions re-dissolved during hypoxia. Consequently, the sediment showed a total acidity neutralization capacity of 3.34 mol/m$^2$/y, with Al, Fe, and proton removal accounting for 55%, 30%, and 13% of this capacity respectively. Compared with coastal marine environments, metal fluxes were up to two orders of magnitude higher, and the sulfur system was the major redox control, meaning that SO$_4$ was the major oxidant of OM and S(II) was the major O$_2$ consumer, with values near 90% in both cases.

Relative HDO and HDCO abundances w.r.t. total hydrogen.

Potential significance of sulfide mineral oxidation for the Cenozoic carbon cycle

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A climatic control on the rate of CO2 consumption by silicate weathering is thought to stabilize Earth’s climate over geologic timescales. At the same time, the observation that tectonic uplift accelerates weathering rates suggests that mountain building can profoundly affect the carbon cycle and global climate. Extensive uplift of mountain ranges during the Cenozoic is thought to have increased silicate weathering rates as evidenced by the marine isotopic records of Sr, Os, and Li, which all show dramatic changes from ~40 Ma to present. Without a corresponding input of CO2, increased silicate weathering fluxes would deplete the atmosphere of all CO2 within a few million years, a clearly unreasonable scenario. While a variety of hypotheses have been put forward in order to balance the Cenozoic C cycle, none of them appear to adequately describe the observations. As such, reconciling this “Cenozoic carbon-weathering paradox” has been a major and as yet unresolved challenge in geochemistry and Earth history. We hypothesize that Cenozoic uplift, in addition to increasing rates of CO2 drawdown by silicate weathering, increased rates of sulfide oxidation coupled to carbonate dissolution. This provided a transient source of CO2 that contributed, at least in part, to the relative stability of Cenozoic atmospheric pCO2. The feasibility of this hypothesis is tested in two ways: (1) a simplified mass balance model that constrains the duration of transient CO2 release in response to increased rates of sulfide oxidation and (2) an inverse isotope mass balance model that uses the Cenozoic isotope records of Sr and Os to reconstruct changes in silicate weathering and sulfide oxidation rates. Together, these models show that the contrasting residence times of DIC and SO4^2- is sufficient to allow for CO2 release over 40 Myr timescales and that modeled rates of silicate weathering and sulfide oxidation are consistent with independent proxy records of paleo-pCO2.

On-site porewater measurements of Lake Baikal sediments

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The extraction and analysis of sediment porewater is crucial to investigate the unique early diagenetic processes in Lake Baikal, the worlds largest and deepest freshwater source. Investigation of the intricate sedimentary Fe/Mn layers requires porewater sampling and analysis with high spatial resolution and high yield of chemical parameters. Transporting the sediment samples from the field to the laboratory is logistically laborious, and prone to contamination, temperature changes, outgassing, mixing, diffusion and redox changes. Therefore, on-site methods are to be preferred.

Here we present an on-site application of a high spatial resolution porewater sampling and analysing method. The facility, combining filter tube sampler and a portable capillary electrophoresis instrument, was set up in a container on the shore of Lake Baikal for the immediate porewater sampling and analysis after coring from the ice.

The extraction of one porewater sample and the detection of its major inorganic cations and anions including the nutrients P and N could be accomplished in less than 15 minutes. The disturbance of the sediment was minimal and oxygen-sensitive reduced iron (Fe(II)) was detected within the set of cations, including Li^+, Na^+, K^+, Mg^2+, Ca^2+, NH4^+, and Mn(II) without splitting, acidification or dilution of the sample. The equipment is inexpensive, easy to handle and to transport.
Tungsten isotope Heterogeneities in Archean Komatiites

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Recent studies demonstrated that the short-lived $^{182}\text{Hf}-^{182}\text{W}$ isotope system ($t_{1/2} \sim 9$ Myr) is a valuable tool for exploring key processes in the early evolution of the Earth, such as mantle differentiation by magma ocean crystallization or crustal extraction and late accretion [1, 2, 3]. The 3.8 Ga Isua rocks [1], the 2.8 Ga Kostomuksha komatiites [2] and the Nuvvuagittuq supracrustal rocks [3] have ~15 ppm $^{182}$W excesses, which is similar to the predicted W isotope composition of the mantle prior to late accretion. However, the mantle source of Kostomuksha komatiites has HSE contents similar to that of the PM estimates, which is inconsistent with preservation of a pre-late accretionary mantle reservoir. Instead, their mantle source must contain an old component, which formed by magmatic differentiation or metal-silicate equilibration and, as a result, inherited a high Hf/W ratio during the lifetime of $^{182}\text{Hf}$.

Here, we present new high-precision W isotope data for 3.3 Ga komatiites from the Weltevreden formation of the Barberton Greenstone belt and 2.4 Ga komatiites from the Vetreny belt. All Vetreny komatiites show small $^{182}$W excesses that average +6.2±4.5 ppm (2σ SD, n = 5). At present, no $^{182}$W anomaly can be resolved in the Weltevreden komatiites ($\mu^{182}$W = -4.1±4.7 ppm, n = 2). Similar to 3.5 Ga Komati komatiites [2], the Vetreny and Weltevreden komatiites have W isotope compositions close to that of the modern mantle, consistent with mantle sources having received most of the terrestrial complement of late accreted material, as indicated by the relatively high calculated HSE abundances in their mantle sources (~80% of the PM estimates, [4, 5]). There is therefore no evidence for a gradual increase of late accreted material contribution in the mantle sources of Archean komatiites from 3.5 Ga to 2.4 Ga, in contrast to earlier conclusions [6]. Our new data rather suggest that most late accreted materials were delivered to Earth and homogenized in the deep mantle prior to 3.5 Ga.


Seasonal and interannual evolution of the monoacids organics in the atmosphere of the humid savanna of Lamto

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This work was made within the framework of the network IDAF. It concerns the follow-up of the acidity of the atmosphere of an ecosystem of wet savanna from the organic fraction of the free acidity. It is a question of understanding the major factors which cause the variability of this organic acidity in the interannual and seasonal scales. During ten-year period (1995-2004) 860 rainy samples were collected in the wet savanna of Lamto. By using Henry’s law, we determined the contents in the air of major organic monoacids (HCOOH and CH$_3$COOH) from the concentrations of these acids measured in rains. The annual partial pressure of organic monoacids on the decade is extremely variable. It is 0.675 ± 0.56 ppb and of 0.413 ± 0.14 ppb respectively for the formic acid and for the acetic acid. This strong variability is bound to their various sources which are also very variable from one year to the next. The organic acidity varies from 40 % to 60 % on average and almost stable rest from a season to the other one. The seasonal analysis shows that generally the partial pressures of organic acids are of a factor twice as raised in dry season that in wet season. This difference is not inevitably connected to the quantity of haste registered from a season to the other one. But would more be connected to the biomass burning which contribute from 21 % to 51 % to the formation of organic acids in the wet savanna of Lamto.
Reactivity of natural heterogeneous nanoparticles

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The chemodynamics of metal complexation by humic acid (HA) is not well predicted by molecular concepts. HAs are small permeable particles with radius of a few nm. They carry a significant negative charge at ambient pH and are important complexes of metal ions in the environment. HAs are physically and chemically heterogeneous with distributed thermodynamic and kinetic properties. Recently developed theory for permeable charged nanoparticles [1-3] is applied to interpretation of metal ion binding by HA. Two opposing electric effects are operational with respect to the overall rate of association, namely (i) acceleration of metal ion diffusion from the bulk medium by the negative electrostatic field of the humic particle, and (ii) accumulation of metal ions in the negatively charged particle body by Boltzmann partitioning. The rate-limiting step in the metal-humic complex formation process is identified by comparing theoretical values of the rate constants for outer-sphere and inner-sphere complexation, with those derived from measurements of the thermodynamic stability constant (K) and the dissociation rate constant (k_d). The experimentally derived association rate constant, k_a, is found to be practically independent of the degree of metal ion complexation, which confirms previous assumptions that the distribution in K is reflected in that of k_a. For the rapidly dehydrating Cu^{2+}, at an ionic strength of 0.1 mol dm^{-3}, the rate of diffusive supply of metal ions towards the humic particles is comparable to the rate of inner-sphere complex formation, indicating that both processes are significant for the observed overall rate. As the ionic strength decreases, the rate of diffusive supply becomes the predominant rate-limiting process, in contrast with the general assumption made for complexes with small ligands that inner-sphere dehydration is the rate-limiting step. The results are highly significant for interpretation of chemodynamics of metal complexation by HA.


Halogen ratios in kimberlites and their xenoliths related to their origin

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Recently, halogens are revealed to be one of the powerful tracers for water cycling in subduction zones [e.g., 1]. In the previous conference, we reported analytical method and some data for Cl, Br and I in kimberlites from South Africa, Greenland, Canada, Brazil, Russia and China, and found that the I/Br ratios of kimberlites are classified into two groups. In this study, additional samples of kimberlites and mantle-derived xenoliths collected from South Africa and Russia were analyzed to investigate the halogen characteristics and their origins in the kimberlite source regions. We analyzed halogens by using the pyrohydrolysis method [2] combined with ICP-MS and ion chromatography.

The kimberlite and xenolith samples from South Africa, Greenland, Canada and Brazil (Group S) showed high I/Br ratios (about $1 \times 10^3$). The value is fairly similar to that of CI chondrite (I/Br ratio: about $1 \times 10^{-1}$ [3]), suggesting these kimberlites preserve the characteristics of primordial halogen in the mantle from which the kimberlite magmas were formed. In contrast, both Chinese and Russian kimberlite and xenolith samples (Group C) showed low I/Br ratios (about $6 \times 10^{-3}$). Similarly low I/Br ratios have been observed in fluid inclusions in eclogites derived from seawater-altered oceanic crust [4] and in seawater associated with halite precipitation [5]. This suggests an involvement of seawater-derived halogens having low I/Br ratios in the source regions of the Group C kimberlites. Low I/Br ratios found in xenoliths also indicate possible subduction-related metasomatism on the halogen composition of the subcontinental lithospheric mantle.

**Chemical weathering in glacial and proglacial environments**

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Physical weathering in glaciated environments initially produces debris which is fine-grained (predominantly silt-sized) and coated in microparticles. Geochemically reactive phases, such as carbonates and sulphides, are liberated from the interior of silicate mineral masses and so become more readily available for chemical weathering. Chemical weathering in glacial environments is microbially mediated, since ingress of atmospheric gases to glacier beds and water-laden rogalglacial sediments is often limited. Instead, the protons required to push chemical weathering beyond simple hydrolysis reactions are generated from the oxidation of sulphides and organic matter. This is the case beneath smaller glaciers, and appears to be the case beneath ice sheets, from waters sampled either directly or indirectly to date. A fundamental difference between the chemical weathering regimes beneath larger and smaller ice masses is the residence time of water beneath the larger ice masses. It is more likely that low oxygen and anoxic conditions are found beneath ice sheets than beneath smaller glaciers. Hence, it is likely that Fe-rich, anoxic waters will be found beneath sectors of the Antarctic and Greenland Ice Sheets. Such waters have the potential to act as fertilisers of Fe-poor circumpolar seas. Chemical weathering is not limited to the aquatic zones that underlie the ice sheets. Movement of ice over bedrock produces localised pressure melting, and the regelation waters produce micro-chemical weathering environments that allow oxidation of sulphides by oxygen, and the formation of nano-particle iron oxyhydroxides. The refreezing of these waters back onto the glacier sole traps basal debris, which, following ice berg calving at the ice sheet margin, transport potentially labile Fe further afield into the surrounding sea. Glacial debris is also a source of labile P to aquatic ecosystems. Finally, a spectrum and surface and basal processes result in glacial runoff often containing labile DOC and DON. Hence, glaciers and ice sheets are currently being thought of as biogeochemical reactors that convert relatively bedrock into a cocktail of relatively labile, potentially bioavailable, nutrients.

The chemical weathering of proglacial sediments too has potential to effect global nutrient and geochemical cycles. Recent work of potential impacts on the global P cycle is reviewed.

**Technetium Reduction and Permanent Sequestration by Formation of Low-Solubility Sulfide Mineral Phases**

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Under anoxic conditions, soluble 99TcO4− can be reduced to less soluble TcO2•nH2O, but the oxide is highly susceptible to reoxidation. One way to minimize the mobility of the TcVII oxyanion pertechnetate (TcO4−) is to effect reduction under sulfidogenic conditions (generated abiotically by Fe0 or biotically) to form TcSx, which is significantly slower to oxidize than TcO2•nH2O. Here we investigate a novel strategy for remediation of Tc-contaminated groundwater whereby sequestration as Tc sulfide is favored by sulfidic conditions stimulated by nano zero-valent iron (nZVI). Fundamental aspects of this hypothesis have been investigated using batch and column experiments under abiotic and biotic conditions.

In the abiotic batch experiments, nZVI was pre-exposed to increasing concentrations of sulfide in simulated Hanford groundwater for 24 h to mimic the onset of aquifer biotic sulfate reduction. Solid-phase characterizations of the sulfidated nZVI confirmed the formation of nanocrystalline FeS phases, but higher S/Fe ratios (> 0.112) did not result in the formation of significantly more FeS. The kinetics of Tc sequestration by these materials showed faster Tc removal rates with increasing S/Fe between S/Fe = 0–0.056, but decreasing Tc removal rates with S/Fe > 0.224. The more favorable Tc removal kinetics at low S/Fe could be due to a higher affinity of TcO2•nH2O for FeS than iron oxides, and electron microscopy confirmed that the majority of the Tc was associated with FeS phases. X-ray absorption spectroscopy revealed that as S/Fe increased, the pathway for Tc(IV) formation shifted from TcO2•nH2O to TcSx. The most substantial change of Tc speciation occurred at low S/Fe, coinciding with the rapid increase in Tc removal rate. This agreement further confirms the importance of FeS in Tc sequestration. The inhibition of Tc removal at high S/Fe appears to have been caused by excess HS−, which, however, is expected to be mitigated under natural conditions due to the abundance of iron oxides that can scavenge sulfide. The reoxidation kinetics of Tc sequestered under sulfidic conditions was significantly slower than that under non-sulfidic conditions, confirming that Tc(IV) sulfide is more resistant to oxidation than Tc(IV) oxide.
Diagenesis, deformation mechanisms and architecture of the fault zones in the extensional Neogene basins of the northeast Iberian Peninsula.

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The faults limiting the Vallès and Penedès basins affect Hercynian crystalline rocks, Triassic, Jurassic and Cretaceous carbonates, and Miocene carbonates, evaporites and detrital rocks. These faults generate gouges, cataclasites, breccias and pseudotachylytes. The main cements are calcite, quartz, laumontite, muscovite, chlorite, albite and iron oxides, depending on the PT conditions. We have established four tectonic events that gather different deformation phases.

Applying geothermobarometers in neoformed chlorites and K-white micas, we have established the PT paths from Hercynian to Neogene. We have observed how the faults have controlled the thickness and distribution of sediments during the first Mesozoic rifting.

Dolomitization and karstification are two widespread diagenetic processes that are recurrent through time and are clearly related to faults.

Trace elements together with radiogenic and stable isotopes of the calcite cements in veins have allowed us to constrain the origin and regime of fluids and the fluid pathways through time.

Isotope characteristics of the Bon Accord oxide body, Barberton greenstone belt, South Africa

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The Bon Accord oxide-silicate body (BAOS) in the the Barberton greenstone terrane is associated with ultramafic igneous rocks. It initially attracted interest because of its extreme whole rock NiO enrichment (>30%) and very unusual mineralogy: In the 1960s, de Waal1-5 described several new minerals, including the Ni end-members of magnetite (ferroan trevorite) and olivine (liebenbergite). De Waal6 identified five zones in the semi-circular body, with an increase in hydrous phases from a massive central portion (mainly containing nepouite and trevorite) to the schistose rim. On the grounds of petrographic information, he proposed that the BAOS represents an altered Archean meteorite.

Tredoux and co-workers' re-examined samples of the BAOS body (sadly no longer in situ) in the 1980s, concentrating on its geochemistry. They rejected the meteorite model in favour of a terrestrial model, because of (a) similarities between chromites in the BAOS and those in the host ultramafite, (b) the possibility that this host rock is potentially associated with the basal part of the Jamestown ophiolite8 and thus would not have been at surface in the Archean, (c) the high concentrations of platinum-group elements (PGE) which are usually relatively low in Ni-rich irons, and (d) positive (unmeteorite-like) trends of PGE patterns9 of many of the BOAS samples.

Radiogenic isotope ratios point to extensive, and variable, degrees of disturbance1, but the U-Pb and Sm-Nd data hint at an Archean (3.5 Ga) age. The Cr isotopes, when normalized to a terrestrial standard, yield a value of 1, within analytical error, which points to a terrestrial source for the material.


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Non-Complexing Anions for Raman Microprobes under Hydrothermal Conditions

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Small scale techniques based on the use of diamond anvil cells (DAC) and capillary cells (“high pressure optical cells”, HPOC) are being increasingly employed to study subcritical and supercritical solutions using Raman spectroscopy [1]. Quantitative Raman measurements to determine thermodynamic properties and structural information often require the use of internal reference standards. These must be soluble, non-complexing and stable under hydrothermal conditions. The species used for this purpose at ambient conditions are bisulfate (HSO4–), perchlorate (ClO4–), perrhenate (ReO4–) and triflate (CF3SO3–).

This paper reports the thermal stability of these internal standards as a function of pH up to 420 °C and 30 MPa. Time-dependent reduced isotropic Raman spectra were obtained using a custom-made LabRamHR 800 spectrometer with quartz HPOC capillary cells at 30 MPa. Typical spectra are shown in Figure 1. In neutral solutions, perchlorate, perrhenate and triflate are stable up to 140 °C, 200 °C and 400 °C, respectively. Simple rate equations, criteria for selecting reference anions, and measurement practices for quantitative hydrothermal studies in Raman microprobes are presented.

Figure 1. Raman spectra showing 0.1 m CF3SO3– decomposition: a) 350°C pH 2 and b) 400°C neutral conditions.


Quantifying the open-system behavior of cosmogenic noble gases in quartz

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Simultaneous production and diffusion of cosmogenic noble gases in minerals at the Earth’s surface offers a potentially powerful tool for reconstructing past Earth surface temperatures. In order to utilize this open-system behavior for paleothermometry, knowledge of both the production rate and diffusion kinetics of a particular cosmogenic nuclide-mineral pair is required. We investigated the diffusion kinetics of 3He and 21Ne in quartz through a series of stepwise heating and degassing experiments. Natural and synthetic quartz samples were irradiated with protons to produce uniform distributions of 3He and 21Ne through similar nuclear transmutations as those induced by cosmic rays. Single grains of irradiated natural quartz exhibit two stages of linear Arrhenius behavior for both He and Ne diffusion: one at low temperatures and for gas release fractions of ~75%, and one at high temperatures for the remaining ~25%. We interpret these two Arrhenian arrays to represent multiple diffusion domain-type behavior in quartz and will discuss the physical meaning of such domains through ongoing experiments on synthetic and natural quartz. Comparison of degassing experiments on vein quartz from the Transantarctic Mountains, conducted using both cosmogenic 3He from a several-hundred grain aliquot and proton-induced 3He from a single grain, demonstrates the following: (i) <6% of the cosmogenic 3He produced within the low retentivity domain is retained at subzero temperatures over several Myr of exposure, while (ii) >90% of 3He is retained within the high retentivity domain. A simple exposure history for this sample using a two-domain diffusion model suggests a maximum effective exposure temperature of -14°C, although 10Be and 21Ne measurements suggest a more complicated history involving both burial and exposure. In contrast, the measured diffusion parameters for Ne from all experiments suggest quantitative retention in quartz over millions of years and at effective exposure temperatures less than 45°C. The ratio of cosmogenic 3He to 21Ne in quartz may therefore be useful for studying the temperatures of surface processes in polar environments.
Impacts of CO₂ perturbation on well composite samples: experiments and numerical simulations

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Abandoned wells in the depleted reservoirs envisaged to host CO₂ geological storages are the main possible leakage pathways of CO₂ towards shallow aquifers. Then, for impact assessment, the alteration of well materials with CO₂ in the reservoir conditions requires to be characterized.

Here, the interaction of a composite well sample – formed of steel casing, surrounded by Portland cement, itself surrounded by sandstone – with wet CO₂ and CO₂-saturated brine under pressure and temperature controlled conditions was studied combining a set of batch experiments [1] and reactive transport modeling. In the experiments, lasting up to 8 weeks, noticeable mineralogical changes were observed in the cement, at the interface with the sandstone, leading to a carbonation of the cement. Main mineralogical changes consisted in dissolution of portlandite, replacement of CSH phases rich in Si by Ca-rich CSH phases and precipitation of calcite, amorphous silica and zeolite [1]. Interestingly, no re-dissolution of calcite was observed at the outer boundary of the cement, in relation with the penetration of the carbonation front, as observed in experiments involving only cement and CO₂-saturated brine [2]. For the two other components of the composite well samples, few changes were observed. The steel showed a moderate corrosion with some precipitations of Fe-oxides at its surface. No changes were observed in the sandstone.

These changes in mineralogy were reproduced with the reactive transport model, which highlights the successive dissolution/precipitation reactions. A good agreement was also obtained with the brine composition evolution record during the experiment. It is worth noting that the model suggested slight mineralogical changes in the sandstone consisting in dissolution of carbonates at the boundary of the sample, in direct contact with the CO₂-saturated brine. This observation, in link with the experimental observations in the cement, indicate a buffering effect of the rock on the CO₂ perturbation. This possible buffering was observed by observations at a larger scale on industrial analogue well samples [3] and suggests a preservation of the well integrity.


Benthic nitrogen fixation and Mn/Fe reduction in the Mauritanian oxygen minimum zone: Two overlooked processes?

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Oxygen minimum zones (OMZ) are currently in the focus of many marine biogeochemical studies, especially since their spreading has been discovered and associated with climate change. Understanding element cycling of OMZ is an important key to predict dynamics of this systems as well as feedbacks to environmental changes. Nitrogen and iron are two central elements in cycling processes of OMZ; however, budgeting and following the fate of these elements still remain challenging. Here we present two benthic processes, microbial N₂ fixation and Mn/Fe reduction, from the Mauritanian OMZ, which were measured at six stations along a depth transect between 50 and 1100 m water depth. N₂ fixation was deduced from nitrogenase activity via the acetylene reduction method. Mn/Fe reduction was measured indirectly via total anaerobic production of dissolved inorganic matter after subtraction of sulfate reduction activity. Highest integrated nitrogenase activity (~360 µmol C₂H₄ m⁻² d⁻¹ down to 20 cmbsf) and Mn/Fe reduction (~29 mmol m⁻² d⁻¹ down to 10 cmbsf) was found within low oxygen zones (45 to 56 µM O₂) beneath sulfidic conditions during organic matter degradation. The percentage of Fe/Mn reduction in total anaerobic organic matter degradation in the top 10 cm increased from ~65% to over 90% downslope. We are convinced that both processes play an important role for element budgeting of OMZ and should be considered in future studies. Especially in developing OMZ featuring terrestrial dust/iron input to the seafloor, such as the Mauritanian OMZ, iron reduction could play a key role for delaying the buildup of sulfidic conditions during organic matter degradation.

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Boninite-derived mafic-ultramafic intrusives from Northern Victoria Land (Antarctica): Implications for mantle source metasomatism

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The Cambrian mafic-ultramafic sequence from Niagara Icefalls area in Northern Victoria Land represents a rare case of boninite-derived intrusive complex. The sequence mostly consists of dunites, orthopyroxenites, melanorites and gabbrororites, locally associated with hornblende granitoids that were most likely emplaced at upper levels of the continental crust. The mafic-ultramafic sequence was interpreted to be formed by boninite-type melts according to the fractional crystallization evolution: olivine → orthopyroxene → orthopyroxene + plagioclase ± clinopyroxene. The concentrations of incompatible trace elements in the whole sequence are extremely low (e.g., TiO2 (0.06 wt%, Y < 3 ppm). The whole-rock REE chondrite-normalized patterns vary from slightly depleted to enriched in the LREE (LaN/SmN = 3.5-0.5), in agreement with the REE variations observed for the included clinopyroxenes. The initial ɛNd of the mafic-ultramafic sequence spans one order of magnitude, which roughly decrease with increasing LaN/SmN. The granitoids associated with the mafic-ultramafic sequence have nearly homogeneous trace and Nd-Sr isotopic compositions. In particular, the granitoids have high REE amounts, with LREE-enriched patterns (LaN/SmN = 4.3-3.4), and highly radiogenic initial Nd-Sr values. The highest initial ɛNd and the lowest initial ɛSrSr (0.7035) of the mafic-ultramafic sequence document the involvement of isotopically depleted asthenospheric sources. The whole-rock Sm-Nd isotopic compositions of the felsic dykes and the hornblende gabbros define a Jurassic isochron with a MORB-type initial 143Nd/144Nd ratio. The δ18O of the hornblendes and coexisting zircons from these rocks do not decipher the presence of a seawater component in these melts. We propose that the felsic dykes and the hornblende gabbros formed by SiO2-rich silicate melts derived from high degree fractional crystallization of MOR-type basalts.

High temperature alteration of the gabbroic oceanic crust (Ligurian ophiolites, Italy): Evidence for hydrothermal-magmatic interactions

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The gabbroic bodies from the Jurassic Ligurian ophiolites are structurally and compositionally similar to the gabbroic sequences from the oceanic core complexes of the Mid Atlantic Ridge. The high temperature cooling evolution the Ligurian gabbros is locally associated with formation of hornblende-bearing felsic dykes and hornblende vein networks. The hornblende veining is correlated with widespread development of hornblende as coronas/pseudomorphs after the igneous clinopyroxene in the host gabbros. We also found hornblende-rich gabbros as dykes/sills within mantle peridotites. The hornblendes from the felsic dykes and the hornblende gabbros are characterized by low Mg#, CaO and Al2O3, negligible Cl, and high TiO2, K2O, REE, Y, Zr and Nb. The whole-rock Sm-Nd isotopic compositions of the felsic dykes and the hornblende gabbros define a Jurassic isochron with a MORB-type initial 143Nd/144Nd ratio. The δ18O of the hornblendes and coexisting zircons from these rocks do not decipher the presence of a seawater component in these melts. We propose that the felsic dykes and the hornblende gabbros formed by SiO2-rich silicate melts derived from high degree fractional crystallization of MOR-type basalts. The vein and the coronitic/pseudomorphic hornblendes show high Mg# and CaO, significant Cl and low TiO2 and K2O. The coronitic/pseudomorphic hornblendes have trace element compositions similar to those of the clinopyroxenes from the gabbros and δ18O close to that of seawater, thereby documenting an origin by reaction between migrating seawater-derived fluids and the host gabbros. The vein hornblendes commonly show slight LREE enrichment and relatively high values of Nb and δ18O. The crystallization of these hornblendes most likely required the involvement of both seawater and magmatic components.
FASTREACT – Efficient reactive transport modelling for long-term repository safety assessments

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Reactive transport modelling is commonly used to provide support for repository engineering activities and safety assessment studies [1]. Yet, the very large temporal and spatial scales involved in these types of studies along with the non-linearity of the underlying processes pose formidable computational challenges that usually force modellers to simplify the problem.

In this work, we present a numerical tool, denoted as FASTREACT, for the efficient solution of large-scale reactive transport simulations. The tool, which relies on the theory of Stochastic-Convective models [2], decomposes complex three-dimensional geometries into a set of independent streamlines. Reactive transport processes are then solved over the whole set of streamlines using one single reference streamline. Reactive transport processes are then solved over the whole set of streamlines using one single reference streamline. Reactive transport processes are then solved over the whole set of streamlines using one single reference streamline. Reactive transport processes are then solved over the whole set of streamlines using one single reference streamline.

The methodology is tested against a synthetic case study where a radionuclide transport problem is solved over a set of heterogeneous conductivity fields. The results compare favourably with those obtained using an Eulerian approach whereas the computational performance of FASTREACT is proved to be much more efficient when compared with the “traditional” Eulerian 3D simulations.


High-precision Neodymium isotope analyses by MC-TI-MS

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Resolving Nd isotope anomalies at the ppm level for materials with a wide range of compositions and Nd concentrations is key to unraveling fundamental relations in geochronology, geochemistry, cosmochemistry and environmental sciences. Nd isotope Thermal-Ionization Mass Spectrometry (TIMS) has proven successful in running Nd both as Nd+ on multiple filament assembly (300-500ng) [1] and NdO+ on single filament assembly (1-10ng) [2].

The present study on a Thermo Scientific TRITON Plus instrument assesses precision and accuracy of Nd analyses adapting the above mentioned protocols on two Nd standards (Merck # 170335 and JNdI [3]) for sample loads ranging from 0.5µg to the ng range, using 1011Ω amplifiers, automatized mode and shortened analysis time compared to literature. Nd+ analyses of 500ng and 100ng loads on double Re filament assemblies in static mode with rotation of the amplifier-cup association (“virtual amplifier”) yield indistinguishable isotopic ratios. The 1-yr 2RSD reproducibility R for (Nd+/144Nd ratios expressed in ppm: R143 = 5 and R142-150 = 4 to 21 (n=70, 3.6-105142Nd+, 100 or 500 ng). Notably, analyses with 10V 142Nd+ ion beams could be limited to 1hr. NdO+ analysis of 10ng loads on single Re filament assembly, a different ion-beam setting, in static mode, yields Nd isotopic ratios indistinguishable from those obtained in Nd+ analyses. This validates the stability of the instrument ion optics, the Faraday cups, and the current amplifier system, as well as accurate oxide interference correction. The 2RSD reproducibility expressed in ppm: R143 = 16 (n=13, 1.5V 143Nd16O+). Notably, one analysis was limited to 25min.

With acquisition times ≤90min and a reproducibility on 143Nd/144Nd of 5ppm (Nd+) and 16ppm (NdO+), this study holds promise for achieving highly reproducible results with ever smaller sample amounts. A TRITON Plus Nd+ study on 100 pg loads using 1012Ω amplifiers reported 2RSD reproducibility of 176 ppm on 143Nd/144Nd [4]. Detection limit, precision and accuracy of Nd isotope TIMS analysis are thus expected to be further improved by the combined use of 1012Ω amplifiers and NdO+ analysis.

Geochemistry and Re-Os age for black shales from the Cambrian-Ordovician boundary, Green Point, western Newfoundland

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Chemical and isotopic signatures for black shales can serve as proxies for reconstruction of paleoenvironmental conditions. Here we bring Rock-Eval, major and trace elements and Re-Os isotopic data together to examine the environmental record at the Cambrian-Ordovician Global Stratotype Section and Point (GSSP) at Green Point in western Newfoundland. The Green Point shales are oil mature and contain Type-II organic material of marine origin. A Re-Os isochron for these shales provides the first depositional age for the GSSP boundary at 484 ± 16 Ma (2σ; Model 3 age; MSWD = 21; n = 13), with an initial 187Os/188Os ratio of 0.74 ± 0.05.

Factor analysis of the geochemical dataset for Green Point shales shows association of most trace elements with TOC and S contents, ensuring an authigenic origin for most elements and hence, their validity for evaluating paleoredox state. Relatively high enrichment factors for redox-sensitive elements (e.g., Re, U and Mo) compared to average shales, but lower enrichment factors relative to modern Black sea sediments, suggest deposition in anoxic waters. Comparison of global Cambrian-Ordovician shale geochemistry datasets leads us to suggest that anoxic conditions and warm oceanic regimes were restricted to the margins of Laurentia and Baltica whereas depositional basins with colder waters (e.g., Avalonia and Gondwana) show geochemically less reducing conditions. These outcomes underscore the important role of paleogeography in regulating ocean conditions and marine life.

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Nanoparticle interactions with lipid bilayers studied by nonlinear optics

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The goal of this work is to understand the fundamental chemistry of how nanoparticles (NPs) interact with biologically relevant interfaces in situ at the molecular level. Surface specific nonlinear optical spectroscopies, namely second harmonic (SHG) and sum frequency generation (SFG), are used to investigate the interactions of NPs with lipid bilayers as model cell membranes. Specifically, SHG allows us to probe binding interactions, while SFG allows us to investigate the effect of NPs interactions with the molecular structure of the lipids.

We use resonant and nonresonant SHG to quantify binding constants, adsorption free energies, and interfacial charge densities in real time for gold NPs and quantum dots interacting with bilayers of various lipid compositions. We also examine the relationship between the measured adsorption free energies and the electric double layer interfacial potential to determine the change in the charge state of the NPs during these interactions. Combining this knowledge with the SFG results, detailing molecular structural changes due to the NP-membrane interaction, allows us to predict possible pathways for the molecular level NP-lipid bilayer interactions.

The impact of lipid composition, NP core composition, and capping ligand on the NP-membrane interactions is investigated. Understanding how nanomaterials interact with lipid bilayers at the molecular level is important for predicting and controlling molecular interactions of nanomaterials with living systems as well as designing environmentally and biologically sustainable nanomaterials.
Shallow-level magma-sediment interaction and explosive behaviour at Anak Krakatau

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Crustal contamination of ascending arc magmas is generally thought to be a significant process which occurs at lower- to mid-crustal magma storage levels where magmas inherit their chemical and isotopic character by blending, assimilation and differentiation [1]. Anak Krakatau, like many other volcanoes, erupts shallow-level crustal xenoliths [2], indicating a potential role for upper crustal modification and hence late-stage changes to magma rheology and thus potential eruptive behaviour. Distinguishing deep vs. shallow crustal contamination processes at Krakatau, and elsewhere, is therefore crucial to understand and assess pre-eruptive magmatic conditions and their associated hazard potential. Here we report on a multi-disciplinary approach to unravel the crustal plumbing system of the persistently-active and dominantly explosive Anak Krakatau volcano [2, 3], employing rock-, mineral- and gas-isotope geochemistry and link these results with seismic tomography [4]. We show that pyroxene crystals formed at mid- and lower-crustal levels (9-11 km) and carry almost mantle-like isotope signatures (O, Sr, Nd, He), while feldspar crystals formed dominantly at shallow levels (<5 km) and display unequivocal isotopic evidence for late stage contamination (O, Sr, Nd). This observation places a significant element of magma-crust interaction into the uppermost, sediment-rich crust beneath the volcano. Magma storage in the uppermost crust can thus offer a possible explanation for the compositional modifications of primitive Krakatau magmas, and likely provides extra impetus to increased explosivity at Anak Krakatau.


Mixing and progressive melting of deep and shallow mantle sources in the NE Atlantic and Arctic

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NE Atlantic and Arctic MORB and primitive off-rift basalts in Iceland, Jan Mayen and Spitsbergen (late Quaternary alkaline basalts) record variable geochemical interaction between the asthenospheric mantle (AM), material supplied by the Iceland plume and subcontinental lithospheric mantle (SCLM). The SCLM-component was mixed with the local asthenosphere during and shortly after the continental rifting and ocean basin opening. Using combined Sr-Nd-Pb-Os-He-isotope systematics, the Iceland plume can be modelled as a mixture of 70% refractory/primordial lower mantle (LM) and 30% recycled oceanic crust (ROC). Low-degree melts are preferentially from the enriched ROC and SCLM components, before progressive melting gradually consumes more of the LM and AM components.

The modelled ROC/SCLM-ratio decreases markedly from a maximum of about 2.3 at the Reykjanes Ridge, Reykjanes Peninsula and the Southern Volcanic Flank Zone in Iceland, via 1.2 at the Snæfellsnes peninsula, Western Rift Zone and Mid-Icelandic Belt and 0.7 at Jan Mayen and the Kolbeinsey, Mohns and Knipovich Ridges to less than 0.2 in Spitsbergen and along the Gakkel Ridge. These ratios might be slightly overestimated due to a general background level of ROC (HIMU-component) in an otherwise depleted asthenosphere.

The minor element composition of olivine phenocrysts in primitive off-rift basalts in Iceland and Jan Mayen, sampling preferentially the enriched source components, indicates that the SCLM-lithologies are dominantly peridotitic, in contrast to the ROC-lithologies, recording a higher proportion of eclogites and hybridized pyroxenites. The combined Hf-Nd-isotope systematics also discriminate between these two enriched source components.

The high proportion of the SCLM-component in the asthenosphere along the Kolbeinsey, Mohns, Knipovich and Gakkel Ridges reflects the young, narrow and slow-spreading character of the corresponding oceanic basins. These ridges appear to sample mantle sources with higher proportions of locally derived SCLM-material than other mid-ocean ridges.

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Ash-Slag Wastes: the Problem of Recycling

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Technogenic materials form separate and the global problem of modern society. They are a special type of raw material from the one hand and an environmental problem from the another. Most urgent part is the recycling of ash and slag.

Coal of Pechora coal-basin (Russia) is characterised with a relatively high ash content. Pechora coal-basin is represented by almost all types of coal, including coke and anthracite at initial stage. Coals are widely used as a fuel, particularly within the boundaries of the coal-basin (Vorkuta, Inta, etc.). Recycling of solid waste from the combustion of fuel is limited to use as a fertilizer rich in trace elements, as well as export them to the so-called ash field, where the above-mentioned products of combustion are stored for later use.

Ash and slag wastes from thermal power plant (Vorkuta coal deposit) were studied.

The composition of the waste was studied and granular iron ore phase was separated. A hierarchy of its globular structure was made. Iron ore pellets are considered as storage of metals. They can be used after the development of appropriate technologies of extraction and enrichment of [1].

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Ce-Monazite and Y-xenotime solubilities in H₂O-NaF at 800°C, 1 GPa: implicatons for REE transport

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Monazite and xenotime host significant rare earth elements (REE) and are useful for geochronology and geothermometry. Their distribution may be impacted by F-bearing fluids, which enhance solubilities of REE and Y in high-grade metamorphism [1]. To assess this we determined the solubility of synthetic CePO₄ and YPO₄ in H₂O-NaF fluids at 800°C and 1 GPa. We used hydrothermal piston-cylinder and weight-loss methods. Compared to the low solubilities of CePO₄ and YPO₄ in pure H₂O (0.04±0.04 and 0.25±0.04 millimolal, respectively [2]), our results indicate an enormous increase in the solubility of both phosphates with increasing NaF concentration in H₂O: CePO₄ solubility reaches 0.97 molal in 20 mol.% NaF, and YPO₄ shows an even stronger solubility enhancement to 0.45 molal in only 10 mol.% NaF. The greatest relative solubility increases occur at the lowest NaF concentration. The solubilities of CePO₄ and YPO₄ show similar quadratic dependence on NaF, consistent with possible dissolution reactions of: CePO₄ + 2NaF = CeF₄⁺ + Na₂PO₄⁻ and YPO₄ + 2NaF = YF₂⁺ + Na₂PO₄⁻. Solubilities of both REE phosphates are significantly greater in NaF than in NaCl at equivalent salt concentration [2]. A fluid with 10 mol.% NaCl and multiply saturated with fluorite [3], CePO₄, and YPO₄ would contain 1.7 millimolal Ce and 3.3 millimolal Y, values that are respectively 2.1-2.4 times greater than in NaCl-H₂O alone. The results indicate that Y, and by extension heavy rare earth elements (HREE), can be fractionated from LREE in fluorine-bearing saline brines which may accompany granulite-facies metamorphism. The new data support previous indications that REE/Y mobility at these conditions is enhanced by complexing with F in fluids phase associated with metamorphism and subduction [4].

Boron isotope systematics of calcitic gorgonian corals and their response to ocean acidification

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Cold-water corals are thought to be especially susceptible to CO2-driven climate change and ocean acidification given that many live near the aragonite saturation horizon in the deep oceans. Recently, however, boron isotope analysis of aragonitic (scleractinian) cold-water corals revealed their capacity to modulate internal pH and aragonite saturation state at the site of calcification, which enables these species to maintain higher rates of calcification and potentially escape the effects of ocean acidification [1].

Here we investigate the boron isotopic systematics of a suite of calcitic gorgonian corals from a wide range of environments to determine their potential to modulate the pH of the calcifying fluid, their sensitivity to future climate change scenarios, and their utility as archives of seawater pH. These calcitic corals are lower in boron concentration as well as isotopic composition ($^{11}$B) than aragonitic cold-water corals, with $^{11}$B values lying along or near the seawater borate equilibrium curve. This shows that, unlike aragonitic corals, these calcitic species have limited if any ability to modify the calcifying fluid and thereby precipitate their calcitic skeletons close to ambient seawater pH. Serve as an archive of continuous seawater pH over centennial to millennial timescales, is especially important given the lack of continuous long-term records and the need to understand the natural variability of seawater pH on longer timescales.


Impact of As(V) on abiotic reduction of U(VI) by mackinawite

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Arsenic and uranium are commonly found together in areas of historic uranium mining activity because they can be released during the mining of uranium ore. Studying the behavior of these elements together under anoxic conditions is necessary to understand their mobility in natural sediments. Recent studies have shown that mackinawite produced through activity of sulfate reducing bacteria is one of the major reductants of U(VI) in subsurface environments [1]. Although reduction of uranyl species by mackinawite has been shown to occur, the reduction of U(VI)-carbonates or U(VI)-arsenates has not been investigated. U(VI) and As(V) can form uranyl arsenate mineral precipitates or surface precipitates depending on their relative concentrations [2]. This study examines the reducibility of U(VI)-carbonates and U(VI)-arsenates under varying U/carbonate and U/As ratios in the presence of mackinawite.

Anoxic batch experiments were conducted including mackinawite with U(VI) and As(V) at concentrations ranging between 50 to 500 μM, including treatments with 5 mM and 30 mM dissolved carbonate. After 48 hours, mackinawite was collected for analysis by X-ray absorption fine structure (XAFS) spectroscopy to determine speciation and binding environment of U and As. Results showed that the extent of U(VI) reduction was not affected by the formation of U(VI)-carbonato complexes. U(VI) reduction was only shown to be limited by As(V) at concentrations at or above 500 μM, where the formation of uranyl arsenate mineral precipitates is favored. Although little influence of U(VI)-carbonate and U(VI)-arsenate species was observed on U(VI) reduction, As(V) reduction was limited in the presence of all tested U(VI) concentrations due to preferential reduction of U(VI). When remediating natural environments containing both As and U, As(V) does not prevent U(VI) reduction by mackinawite under environmentally relevant concentrations.

Geochemistry and petrogenesis of a nested granite intrusion – the Sedmihoří composite Stock (Bohemian Massif)

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Better understanding of how zoned plutons are constructed and for how long the upper crustal magma chambers remain active is crucial to constrain a range of lithospheric processes, including igneous petrogenesis, ore formation, crustal rheology/deformation and volcanism.

The shallow-level Sedmihoří Stock in the southwestern Teplá–Barrandian Unit, Bohemian Massif, provides an excellent case example of a zoned post-tectonic granitic intrusion. It is roughly circular in plan-view and formed by nested intrusions of three magma pulses within a single conduit: (i) less evolved outer porphyritic Bt monzogranite (326.2 ± 1.2 Ma (2σ), LA ICP-MS Zrn), (ii) more fractionated inner Bt–Mu monzogranite (326.6 ± 1.2 Ma), and (iii) innermost minor Mu leucogranite with Tur. All the varieties are siliceous (SiO2 > 71 wt. %) and moderately peraluminous. While major-element contents do not vary greatly, trace elements display significant differences between the pulses (e.g., LaN/SmN = 4.24–4.45 outer; 3.38–3.44 inner; 2.95–4.43 innermost). Still, each of them preserves its remarkable homogeneity.

Field observations, fabric patterns and geochemistry suggest that each pulse represents a single batch of magma with its own geochemical characteristics and potentially also petrogenesis. This rules out a shallow-level fractionation or contamination by the country-rock metasediments, and points to processes deeper in crust or differences in source materials.

The trace-element compositions with evolved crust-like Sr–Nd isotopic signatures show that the granite pulses were derived by anatexis of immature metasediments (Neoproterozoic metasediments of the Teplá–Barrandian Unit; shown by the presence of inherited components in Zrn 2 and 0.6 Ga old). The higher proportion of pelite within the source of the inner Bt–Mu monzogranite is shown by higher Rb/Sr ratios (9–15) as well as more evolved Sr (ε66Sr/87Sr326 = 0.7098–0.7154) and less radiogenic Nd (ε143Nd = -3.7) than in the outer facies (ε66Sr/87Sr326 = 0.7067–0.7076; ε143Nd = -2.5 to -2.7). Research funding: Czech Science Foundation (GA ČR) P210/11/1168.

Using laser-based technology to quantify carbon-13 ratios and fugitive emission CH4 flux rates quickly and easily

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The United States is home to what is estimated to be the largest known shale gas reserves in the world. Often referred to as the “bridge fuel” that will aid in the country’s energy transition from coal to renewable sources like wind and solar, natural gas production is growing at the fastest pace in U.S. history. This expansion involves the introduction of hundreds of thousands of new natural gas wells and processing facilities all across the U.S. Of primary concern is the potentially damaging impact of natural gas drilling on human health due to increase pollution exposure.

Picarro has developed a new instrument (plume scanner) which uses laser-based technology to measure natural gas fugitive emission flux rates from natural gas facilities quickly and easily. As the plume scanner vehicle drives through the plume at the speed of traffic, the air is sampled at 4 different heights along the axis of the vehicle. These gas samples are continuously stored in the vehicle along with wind and vehicle velocity information. When a plume is detected, the stored gas samples are redirected into the inlet of a cavity ringdown spectrometer where concentration and/or carbon-13 CH4 ratio measurements are recorded, synchronized, and/or processed to produce an intensity map or a so-called “scanned” plume image. In this way, fugitive emission flux rates and isotopic measurements of highly localized sources such as natural gas facilities can be made quickly and easily providing greater transparency to stakeholders.
Rare earth element behavior in subduction-zone fluids: the effect of T and ligands

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Understanding of rare earth element (REE) systematics has a broad application for subduction-zone processes. Particularly, arc-related magmas display a typical trace element abundance spectrum, characterised by the enrichment in light rare-earth element (LREE: La, Ce, Nd) and depletion in the heaviest rare earth element (HREE: Yb, Lu) relative to MORB. This particular geochemical signature may result from the influx of aqueous fluids and/or silicate melts derived from within the slab. Therefore, investigating the behavior of REE in fluids at high P and T conditions is crucial for constraining and within the slab. Thus, this study presents new experimental data on REE solubility in aqueous quartz-saturated fluids, containing various ligands (F-, CO32-, SO42-, Cl-), and in hydrous haplogranitic melt at conditions relevant for subducting slab (600-800 °C, 2.6 GPa). The experiments were conducted in an end-loaded piston-cylinder apparatus and the fluids were in situ sampled at P-T in the form of primary fluid incusions in quartz. Gold capsules were loaded with a chip of synthetic (La,Nd,Gd,Dy,Er,Yb)2Si2O7 – phase, various aqueous solutions (~ 20 wt.%) and a piece of natural quartz. In the case of experiments with melt, the capsule was loaded with a piece of REE2Si2O7, a synthetic haplogranitic glass and water (~15 wt.%). Rb and Cs were added to the solutions as internal standards for LA-ICPMS analyses.

The solubility of REE in quartz-saturated H2O, free of additional ligands, increases more than an order of magnitude as temperature is increased from 600 to 800 °C. Addition of ligands, even in relatively small amounts (0.3-1.5 m), promotes REE solubility compared to pure H2O. Each type of ligands leaves a characteristic REE pattern, reflecting the preferences of REE complexation: e.g., efficient LREE-CI and HREE-CO3 complexation. The solubility of REE in the melt is moderate, comparable with the solubilities in pure H2O.

Our results showed that REE can be effectively transported by aqueous fluid and the effect of temperature as well as fluid chemistry play an important role in REE mobility and LREE/HREE fractionation.

3D shapes of regolith particles: comparison between Itokawa and Moon

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Hayabusa sample analysis elucidated a variety of surface processes on asteroid Itokawa: (1) regolith formation by impact [2], (2) solar wind implantation to uppermost regolith surface [3], (3) space weathering rim formation mainly by solar wind He implantation (~10^3 yr) [4,5], (4) grain abrasion probably by grain motion due to impact-induced seismic waves in a regolith layer (~10^2 yr) [1,2,6], and (5) final escape of particles from the asteroid by impact (<8 Myr) [3]. The grain abrasion was found based on the 3D shapes and surface morphologies of Itokawa samples using x-ray micro-tomography [2] and FE-SEM observation [6]. The 3D shapes of lunar regolith samples were also examine by tomography [7] but not grain-by-grain as performed for the Itokawa samples. In the present study, the 3D shapes of Apollo 16 highland (60501) and Apollo 11 mare (10084) regolith samples were examined by the same method as the Itokawa particles using micro-tomography at SPring-8.

The shape distribution shows that the lunar regolith is more spherical than the impact fragments although lunar regolith is the product of impact on the lunar surface, suggesting that the regolith was abraded. The cause may be grain motion during gardening by impacts. The degree of abrasion is larger than that of the Itokawa particles due to larger scale of impacts and longer regolith residence time.

Influence of aerosols on cloud characteristics over Europe: Study with the meteorology-chemistry-radiation eulerian model.

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Several studies demonstrated that aerosol particles play a crucial role in the climatic system, scattering the incoming radiation (direct effect) and altering cloud properties (indirect effect). Excellent efforts has been done by scientific community to represent the indirect effect in the atmospheric model, but the radiative forcing associated to indirect effect is still very uncertain.

In this study we tried to address the question: how well do the models reproduce the amplitude of aerosol indirect effects? In order to answer to the question, we used WRF/Chem model. A new parameterization for secondary organic aerosol (SOA) yield based on the volatile basis set implemented in WRF/Chem recently, has been coupled with the microphysics of clouds. The effects of this new mechanism is evaluated through the comparison of high resolution simulations on a cloud resolving domain (2 Km of resolution) against the ground-based and aircraft measurements of aerosol chemical composition and particles, and cloud microphysics, issued in the frame of European Integrated project on the Aerosol Cloud Climate and Air Quality Interaction (EUCAARI). The comparison of model results among observations suggest that discrepancies in simulation of chemical fields should be due to errors in simulated meteorological field and uncertainties in horizontal and vertical interpolation of anthropogenic emissions, in their total amount and hourly variations.

The amplitude of indirect has been calculated as $\frac{N}{r_e}$, where $r_e$ is the cloud droplet effective radius and N aerosol particle number of each mode of log-normal distribution. Observations attribute the indirect effect to total aerosol particle number with a value of -0.22, very to theoretical value of -0.23. Instead, WRF/Chem reproduces the observed amplitude of IE, but attributes it to the particles of accumulation, while the observations indicate a strong IE due to total particle number.

The reasons of this results are under investigation.

Formation of monazite-(MREE) from paleozoic shales: Role of host rock chemical composition and organic material

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Rare earth element (REE) distributions of stream water, normalized to upper continental crust (UCC), showed, from the source to the catchment outlet, fractionation patterns from heavy REE enriched to more flat and middle REE (MREE) enrichment, together with a progressive disappearance of a negative Ce anomaly. As a consequence, Pourret et al. [1] suggest that the continental shelf could be considered as a potential REE trap and thus that shelf sedimentary rocks, similar to metalliferous deep sea sediments, represent a REE potential resource and guide for their exploration. The reassessment of the REE potential of France, led us to discuss the behavior of REEs, from the continental shelf to the basin plain, using authigenic monazite occurrences within oredovician shales and black shales from Brittany (France). Monazite grains (up to 2 mm in diameter) are mostly characterized by their grey color, host-rock mineral inclusions, REE UCC distribution patterns enriched in MREE, low Th and U contents, lack of inherited cores, that strongly suggest authigenic crystallization during diagenesis to low grade metamorphism conditions. Chemical composition highlights zoned crystals with MREE enriched cores (up to: 10 wt% Sm$_2$O$_3$, 1.3 wt% Eu$_2$O$_3$ and 5 wt% Gd$_2$O$_3$) and light REE (LREE) enriched rims. Thus grain cores are characterized by negative and low values of log[(La/Sm)$_\text{UCC}$] and high values of Eu whereas rims have slightly negative to positive values of log[(La/Sm)$_\text{UCC}$] with low Eu concentrations. Grey monazite REE$_\text{UCC}$ patterns also reflect the abundance of these elements in shales and black shales. Indeed, at near neutral to alkaline pH, monazite evidenced MREE enriched patterns directly linked to organic matter (OM) content, whereas at alkaline pH, REE speciation is mainly driven by carbonate complexation, resulting in the formation of the LREE enriched monazite. This latter hypothesis will be further tested and reinforced by analysing OM fractions of shales and black shales. Eventually, such monazites were later concentrated within placers @ 2 kg/t.

Nitrogen isotope biogeochemistry of the South Atlantic

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The South Atlantic at 40°S is a highly productive region of the open ocean marking the transition between the Sub Antarctic Zone (SAZ) and the South Atlantic gyre. We present a high resolution depth transect of Antarctic Zone (SAZ) and the South Atlantic gyre. We present the open ocean marking the transition between the Sub Antarctic Zone (SAZ) and the South Atlantic gyre. We present the open ocean marking the transition between the Sub Antarctic Zone (SAZ) and the South Atlantic gyre. We present the open ocean marking the transition between the Sub Antarctic Zone (SAZ) and the South Atlantic gyre.

During NO3 utilization of water masses of subtropical (Agulhas Current, South Atlantic Central Water (SACW)) and Antarctic origin (Antarctic Intermediate Water (AAIW) and Sub Antarctic Mode Water (SAMW)). The preferential uptake of 14N by biota leaves NO3 enriched in 15N as it is utilised; therefore, NO3/15NO3 relationships in combination with nutrient stoichiometry can describe the history of water mass formation at the surface and transformation during transit [1].

The SAMW supplies high nutrient waters to the low latitude Atlantic, fuelling primary productivity [2]. A greater variation in SAMW NO3 and 15NO3 values compared to previous studies [3,4], may result from incorporation of the underlying AAIW and overlying surface waters during transport. At the surface, we estimate isotope fractionation during NO3 utilisation of ε = -9‰, which is consistent with previous SAZ estimates [3]. However, this fractionation effect is diluted in most profiles by the influence of the nutrient poor SACW.

Tropical surface waters are identified between 50-53°W, with 15NO3 values in the range of 4-6‰. These depleted 15NO3 signatures suggest the influence of N-fixation in this water mass. Similarly, the Agulhas leakage into the South Atlantic is characterised by low 15NO3 signatures because it is sourced from the combination of tropical and Southern Ocean water masses of the Indian Ocean. These datasets will be modelled in an attempt to quantify the extent of N fixation, NO3 utilisation and water mass mixing that has occurred in these water masses, to address their role in nutrient transport and productivity within the ocean.


Volcanism on Mars controlled by early oxidation of the upper mantle

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We investigated the genetic relationships between Martian meteorites and the surface rocks of the Gusev Crater analysed by MER Spirit. The SNC meteorites, with crystallisation ages mostly in the range 1.4Ga-180 Ma are likely derived from young volcanic regions such as Tharsis Plateau. They are enriched in volatiles and depleted in Ni and other chalcophile elements relative to terrestrial igneous rocks of similar composition1. Surface rocks from the Gusev crater are much older (~ 3.7 Ga) and are substantially richer in Ni and S with lower Mn/Fe ratios than the meteorites2. These observations lead to doubts that surface rocks and SNC meteorites have similar mantle source regions.

We started with the Dreibus and Wänke (DW) estimate of Martian mantle composition and experimentally-produced partial melts of this mantle at 1.5 GPa (1.3). Martian mantle Ni and S contents (up to 3000 ppm) were varied and the Ni and S contents of the melts calculated assuming sulphide saturation at low fO2 (FMQ - 2 log units). The melts were allowed to fractionally crystallise the liquidus mantle phases (olivine, orthopyroxene, clinopyroxene spinel and sulphide), using the crystallisation program ‘Petrolog’. This yielded the correct SNC trends of Ni-Mg and Mn-Fe for melts and cumulates with mantle Ni content of 1800 ppm. We repeated the procedure at high fO2 (FMQ+3 log units), conditions where sulphide is unstable. Partial melts are much richer in Ni and S and reproduce the Ni-Mg trend of the Gusev crater rocks. Furthermore, magnetite, found in the recently described “Gusev-like” meteorite NWA70341 becomes the liquidus phase and extracts Mn from the differentiates, consistent with observations of surface rocks. Our results demonstrate that the surface basaltic rocks of the Gusev crater and the igneous SNC meteorites are consistent with partial melting and fractional crystallisation from the same DW-like source but under different fO2 conditions. The implications are that Mars’ surface oxidised early in its history and that oxidised material was recycled into the upper mantle.

A new conceptional model: Reconstruction of freshwater incursions in stratified marine paleoenvironments in Late Devonian extinctions

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One of the biggest mass extinctions in Earth’s history took place in the Late Devonian. The most well known event occurred at the Frasnian – Famennian boundary, but there were also major biodiversity crises towards the end of the Givetian and Famennian time periods.

Here we present a novel biomarker approach using methyltrimethyltridecylchromans (MTTCs) as indicators of freshwater incursions and terrigenous input to a Late Givetian/Early Frasnian marine palaeoenvironment [1]. The abundance of gammacerane and Chlorobi biomarkers furthermore indicated persistent water-column stratification and prevailing photic zone euxinia. MTTCs are isoprenoid substituted aromatic compounds which are established palaeosalinity indicators [2]. Nevertheless, their source and formation pathway remain unknown. Our data would be consistent with an origin from early diagenetic condensation reactions of phytol with alkyl phenols (from higher plant sources) as it has been suggested previously by Li et al. [3].


Recent groundwater circulation of U at Forsmark, eastern Sweden

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Uranium in groundwaters commonly shows a trend of decreasing concentration with depth due to the chemical reactivity of recharging waters, rich in O2 and CO2, which promotes U mobility by oxidising U(IV) to U(VI) and by carbonate complexation. Towards depth, the redox potential drops, U is increasingly reduced to the more insoluble U(IV) form, and U concentrations decrease. However, carbonate complexation may enable dissolved U(VI) to exist to greater depths in even mildly reducing conditions. Such is demonstrated in the crystalline bedrock aquifer of the Forsmark area, where elevated U concentrations (10 to 170 µg/L) are found in several borehole sections at depths down to 600 metres. These concentrations are generally associated with Brackish-type groundwaters which are not oxidising but show Eh > −190 mV and bicarbonate contents >30 mg/L. It can, however, be concluded that this water has not transported U into the bedrock aquifer, but rather has mobilised an easily dissolvable uranium phase present along some of the water conducting fractures. The 234U/238U activity ratios (AR) in the groundwaters are within the range 2 to 6 and the samples with the highest U contents tend to show the lowest 234U/238U AR (≤ 3). Annual sampling (from 2005 to 2012) in some borehole sections with elevated U, has shown the 234U/238U AR to be very stable and unique for each specific fracture groundwater and most probably also for the dissolved phase. Because the suspected source is hosted in the fracture fillings, the water/fracture mineral interaction is also studied using U-series measurements on the mineral phase. The results support a complex pattern of leaching and redeposition of U in many of the studied fractures during the last 1.5 Ma, whereas others show only small or insignificant deviations from equilibrium. Together these results support the very inhomogeneous distribution of flow paths typical for crystalline bedrock and previously interpreted in the Forsmark area.

An understanding of the geologically late (<1.5 Ma) behaviour of U in the groundwater can help to interpret the groundwater circulation and find the most important water pathways during this period. The changes in groundwater composition and redox conditions have caused both mobilisation and deposition of U, and it is possible to trace both processes in one and the same fracture sample.
Volatiles released in subduction zones and their role in sustaining magmatism

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It is widely accepted that the generation of arc magmas is triggered by fluids released from the subducting slab and by their interaction with the overlying mantle wedge [1]. The major lithologies involved in devolatilization are pelites, hydrothermally altered basalts, and serpentinized harzburgites. Thermodynamic calculations and experiments predict that HP fluids are dominated by H2O. Nevertheless, the importance of carbon species has been highlighted in the last years because of the relevant CO2 content of arc magmas and the observation of carbon-bearing phases in mantle-wedge peridotites. Experiments have shown that the release of volatiles extends over several tens of km depths and result from a succession of continuous and discontinuous reactions involving hydrous phases in the subducted lithosphere, such as antigorite and chlorite in ultramafics; amphibole, lawsonite, zoisite, and chloritoid in mafic rocks. Phengite and biotite are involved in melting reactions of a variety of bulk compositions whenever K is available. Carbonates once formed are refractory and stable at very high pressures. Therefore, the transport of carbon in the mantle wedge, via solute species in aqueous fluids or via advecting rock masses in buoyant “cold plumes” have been proposed. In the metasomatized mantle wedge, the stability of hydrous phases depends on bulk alkali content, amount of available fluid and possibly the redox state of the system. In COH-bearing systems, the framework of phase relationships is more complex and the position of the solidus is controlled by a number of factors. In fluid-undersaturated COH-systems, the bulk composition (i.e., XCa, XMg, alkalies) and the redox state of the Fe-bearing phases are variables that strongly influence the solidus position. Peridotites saturated in a COH-fluid melt at lower temperatures compared to H2O-free, CO2-bearing peridotites. However, the increase of bulk CO2 shifts the solidus, so that fluid-saturated COH peridotite can eventually melt at higher temperatures compared to fluid-undersaturated COH peridotites. Apparent discrepancies concerning solidus position reflect the variety of experimental strategies adopted, which can be applied to a wide range of geodynamic settings.


The formation of elemental sulfur nodules; A modified ‘thiosulfate shunt’ in unique environments

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Elemental sulfur, also known as ‘native sulfur’, has been found in a range of natural environments, including marine and lake sediments, often forming large nodules or veins, millimeter to centimeter in size. What governs the formation of elemental sulphur nodules remains enigmatic. While most of the literature suggests it is formed by partial re-oxidation of hydrogen sulphide, elemental sulfur can also form during incomplete bacterial sulfate reduction, during sulfur disproportionation, or even during gypsum metamorphism.

We present sulfur isotope ($\delta^{34}S$) and major element data from sulfur nodules and surrounding gypsum, from the Lake Lisan formation near the Dead Sea, Israel. The $\delta^{34}S$ in the nodule is constant between -9 and -11‰, 27 to 29‰ lighter than the surrounding gypsum, consistent with their formation in an ‘open system’. Iron concentrations in the gypsum increase toward the nodule, while manganese concentrations decrease, suggesting a redox boundary at the nodule-gypsum interface during aqueous phase diagenesis. We suggest that sulfur nodules in the Lake Lisan formation are generated through bacterial sulfate reduction, which terminates at elemental sulfur. Sulfate-saturated pore fluids, coupled with the low electron-donor availability, terminate the trithionate pathway before the terminal two-electron reduction, producing thionites, which disproportionate via a modified thiosulfate shunt to form abundant elemental sulfur.
BTX sorption by surfactant-modified synthetic zeolite

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Zeolites are group of aluminosilicate minerals that are distinguishable by their high porosity, high cation exchange capacity and regular cage-like structure. They possess a negative charge that is an effect of heterovalent substitutions of Si4+ by Al3+ in the tetraedra which are the primary building units of the mineral’s framework. Synthetic zeolite was created from fly ash after coal combustion in hydrothermal conditions. Modification of zeolite was conducted with the use of one of the quaternary ammonium salts: hexadecyltrimethylammoniumbromide (HDTMA-Br).

Suspension of synthetic zeolite was mixed with HDTMA solution in high temperature for 24 hours. Surfactant was adsorbed onto a synthetic zeolite in amounts of 1.0 and 2.0 of the external cation exchange capacity (ECEC) in quantities of 24.4 and 48.8 mmol per 100 g of zeolite respectively. Third sample that was used was pure zeolite.

The purpose of this research was to evaluate the difference in sorption of BTX (benzene, toluene, xylenes) on the unmodified zeolite and organo-zeolite modified by HDTMA. Modification in amount of 2.0 ECEC shows higher sorption of BTX then organo-zeolite 1.0 ECEC. Further still, was the unmodified zeolite. This is caused due to high affinity of apolar BTX to the hydrophobic zone of HDTMA chains. The range of BTX concentrations used in this study was limited by their solubility in water.

Additional objective was to investigate whether FTIR could be used in qualitative and quantitative determination of BTX adsorbed by the zeolite. Our study has provided information on presence of particular spectra that correspond to certain organic compound.

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Three-dimensional distribution of anatectic melt inclusions in garnets by X-ray micro-tomography

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X-ray micro-tomography (µCT) has been applied to investigate the three-dimensional distribution of primary melt inclusions in garnets from El Hoyazo (Neogene Volcanic Province, Spain). Modeling the distribution density allows a better understanding of the growth and trapping history of peritectic minerals and coexisting fluids and melts during the partial melting of the crust. Glassy inclusions are trapped in nearly all mineral phases in metapelitic enclaves found within El Hoyazo dacites and they have been extensively analyzed. To better investigate their three-dimensional distribution and to understand the relationship between them, other mineral inclusions and the host phase, two garnets have been imaged through µCT. One of the two was then cut to expose a nearly-equatorial plane to SEM analyses. A preliminary classification based on different absorption coefficients was applied to different inclusions in the tomographic images and then verified by SEM chemical maps. We measured the volume and position with respect to garnet barycenter of glassy melt inclusions and of single-phase inclusions such as monazite, zircon and apatite for a comparison. The modeling reveal a clear peak of melt inclusions density at 1/3 radius distance from the garnet center, while mineral phases are more randomly distributed. Moreover, the type and the size of the inclusions are statistically related to their spatial distribution. There is no evidence of a sharp boundary between inclusion-rich cores and inclusion-free rims. This together with the chemical profile of the garnet composition strongly suggests that the garnet grew in one single event in the presence of anatectic melt. After the maximum, the linear decrease in the density of melt inclusions could indicate trapping at a constantly slowing growth rate of the host mineral or a constant decreasing melt supply. The first hypothesis is less convincing, since mineral inclusions are still trapped after the decrease of melt inclusions, and even seem to increase in density.

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Recycling of water between the mantle and crust/hydrosphere

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Water is added to the mantle via subduction where, due to the break down of hydrous mineral phases, water is released from the subducting slab. Conversely volcanism expels water from the mantle.

To help constrain the water flux of the mantle, we present data from mantle pyroxenes of sub-arc xenoliths and therefore providing estimates of the amount of water recharging the mantle. We have measured the concentration of water within pyroxene phenocrysts from Azores lavas (OIB setting) and the andesitic volcanoes of New Zealand (arc setting).

Preliminary data from pyroxenes of sub-arc metasomatised harzburgite xenoliths reveal varied water concentrations from relatively dry sub-arc mantle regions (Mexico and Kamchatka ~150 ppm) to relatively wet areas (New Ireland and Phillipines >500 ppm). This variation may reflect differences in the petrogenetic history of the xenoliths such as various degrees of metasomatism.

The water content of pyroxenes from Azores lavas vary between 100 and 400 ppm, with the notable exception of relatively hydrous pyroxene cores from Sao Miguel that contain up to 800 ppm.

Preliminary data from pyroxene phenocrysts of Mt Ruapehu and Taranaki (New Zealand) suggest that they also contain a similar variation in water concentrations to that seen within the Azores pyroxenes (between 100 and 450 ppm water). Differences between each andesitic system are also possible with Mt Taranaki (amphibole bearing, back-arc volcanic system) pyroxenes containing relatively low water concentrations (100-250 ppm) compared to the pyroxenes from the volcanic front-arc system of Mt Ruapehu (>300 ppm).

Interestingly pyroxene phenocrysts from OIB and arc magmatism contain a similar range of water contents to pyroxenes from the sub arc mantle.

Extremely young melt infiltration of the continental lithospheric mantle

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It has long been inferred that mantle metasomatism and the incompatible element enrichment of the continents require melts formed by low degree melting of the mantle. Yet establishing the presence of these melts and whether this metasomatism is ongoing and continuous, or spatially and temporally restricted, has proved difficult. Here we report large U-Th-Ra disequilibria in metasomatised, mantle xenoliths from the Newer Volcanics Province in southeastern Australia. The infiltration and passage of carbonatitic ± hydrous silicic melts, combined with crystallization of pargasite can account for the observations. The half-lives of the nuclides indicate that metasomatism was extremely young (≤ 10 kyr) and probably on-going at the time of incorporation in the magmas that transported the xenoliths to the surface. This provides unique evidence for the presence and continuing migration of small melt fractions (~0.02%) in the upper convecting mantle and provides a likely explanation for the seismic low velocity zone. These melts cannot, themselves, be responsible for average continental crust but they could provide an important component for ocean island basalts if returned to the convecting mantle.
Isotopes in vertebrate bioapatite: proxies for climate, pCO2 and diet

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Vertebrates integrate bioavailable elements in their skeletal tissues taken up from the environment via air, water and food. Bones and teeth archive isotope signatures of these elements over the timespan of tissue formation and/or remodelling. This enables the reconstruction of diet (δ13C, δ44/42Ca), climate (δ18O), body temperature (ΔT), atmospheric pCO2 (ΔT′O) and habitat (δ18O, 87Sr/86Sr) from vertebrate fossils. Bioapatite of fossil hard tissues, especially enamel, can preserve original isotope compositions over geological time scales. The isotopes of the two major elements (Ca, O) in bioapatite are least biased by diagenetic alteration.

δ18Oemo of terrestrial and aquatic vertebrates is a proxy for meteoric and ambient water δ18O values, respectively. Enamel δ18Oemo values of fossil large mammals were used to infer the terrestrial palaeoclimate during the last 35 million years for Central Europe. Reconstructed air temperatures agree well with other climate proxy data. The 17O-anomaly (Δ17O) of air oxygen is a proxy for atmospheric pCO2. This anomalous Δ17O of small mammals (<1kg) with a high metabolic rate and thus O2 consumption. It is preserved in fossil teeth and Δ17Oemo can be used as a new proxy for palaeo-pCO2 reconstructions and to monitor diagenetic alteration of bioapatite δ44/42Ca values.

Calcium isotopes (δ44/42Ca) are a very promising deep time diet proxy for fossil vertebrates with a high preservation potential, even in fossil bones. δ44/42Ca values enable us to determine the consumption of plant versus animal tissues and decrease systematically with each trophic level along the foodchain. We found a trophic level effect of -0.4‰ between bones of extant African mammalian herbivores (0.4±0.14‰) and carnivores (-0.89±0.14‰). Ant/termite-feeding mammals (Gastornis) are more in accordance with a herbivorous diet.

Developing speciation codes and thermodynamic data for non-isothermal and non-isobaric systems: applications to CO2 sequestration

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Geochemical models typically simulate geochemical processes using thermodynamic data sets of equilibrium constants calculated 0.01-300°C along the steam saturation curve. This approach is sufficient for a broad range of geologic conditions, as long as the data has been calibrated against calorimetric, field, and experimental measurements. However, some commonly utilized data and methods result in unacceptable uncertainties. Notably, longstanding inconsistencies in the aluminum mineral and aqueous species data that are included in many thermodynamic datasets have not been sufficiently resolved. Moreover, simulations of key geologic processes, such as geologic CO2 sequestration and hydrothermal alteration, are challenging due to the limited T-P range of the data sets.

In this contribution, we correct some of these problems by taking account of recent innovations that enable acquisition of formatted datasets at any T and P within the limits of the thermodynamic equations of state [1]. This is only a short-term measure, however, because modern computers permit development of a new generation of speciation codes that dynamically calculate equilibrium constants at the modeled T-P conditions. These codes will be particularly useful in large-scale, non-isothermal, and non-isobaric reactive transport models. To this end, we develop and use an integrated thermodynamic-speciation code that relies only on standard state thermodynamic properties and equation of state parameters to dynamically calculate mineral-brine-CO2 interactions. The code incorporates a new, calibrated, internally consistent thermodynamic data set for key aluminum minerals and aqueous species as well as literature data for other minerals and aqueous species. Compared with experiments involving a) thermally-driven dolomite dissolution and precipitation and CO2 exsolution, and b) arkose alteration under elevated T, P, pCO2 conditions, the data and integrated speciation code perform well and provide a new opportunity to kinetically evaluate whole-rock dissolution and precipitation reactions.


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Serpeninization is a widespread geochemical process involving the alteration of ultramafic rocks in the presence of water, resulting in a high pH (>10), highly reducing environment containing large quantities of dissolved hydrogen and potentially abiotic organic molecules, which can serve as energy sources for microbes in the subsurface. Habitability models predict that these environments can sustain microbial life, but little work has been done to directly characterize the microbial communities utilizing the energy generated from this process. Furthermore, prior studies of continental serpentinites have sampled surface seeps that represent an interface between end-member fluids and the atmosphere and may not truly represent the extreme conditions encountered deep within the subsurface.

A recent drilling project at the Coast Range Ophiolite Microbial Observatory (CROMO) in northern California has supplied rock cores from up to 40 m below the surface and provided a window into an actively serpentinizing system. Rock cores from two wells, roughly one mile apart, were sampled at various depths and analyzed for microbial community composition via metagenomics and 16S rRNA sequencing, allowing for the comparison of communities within and between rock cores. Additionally, fluid samples from both wells have been sequenced, allowing for the identification of rock-specific microbes within the environment. Preliminary data indicate that communities associated with rocks are lower diversity and different composition than those associated with the surrounding fluids.

To test the question of habitability within the serpentinite subsurface, microorganisms have been cultivated in situ within the monitoring wells, showing growth over time, and their diversity is being assessed via 16S rRNA tag sequencing. Future experiments include providing environmentally-relevant mineral substrates in situ to determine the extent of microbe-mineral interactions within the serpentinite subsurface environment. This work adds to our growing understanding of the role of microorganisms in this extreme environment.

**Rock-Hosted Serpentine Microbiome**

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**Pilbara greenstones revisited: a multi-proxy geochemical perspective on Archean crust-mantle interaction**

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Metabasalt (greenstone) sequences in Archean cratons provide insights into mantle melting and crust formation processes in the Early Earth. The 3.53–3.22 Ga eastern Pilbara Craton, Western Australia, contains large-scale exposures of well-preserved Paleoarchean supracrustal volcanic sequences, which can be correlated over considerable distances and are characterised by virtually undisturbed immobile element (REE, HFSE) systematics. Previous studies have aimed to establish a stratigraphic and chronological framework, reconstruct the tectonic setting for greenstone emplacement, and determine the composition of sources that may explain the chemical/isotopic signatures in these rocks. The recent suggestion of involvement of a Hadean crustal component, based on distinctly negative εNd values in metabasalts and cherts within the Warrawoona Group [1], has motivated us to revisit these issues.

Here we present new high-precision trace element and isotopic (Nd-Hf) results for tholeiitic and komatiitic rocks of the Warrawoona Group, the lowermost section of the East Pilbara terrane. Trace element patterns in our samples are characterized by comparatively flat HREE distributions but wide variations in LREE abundances, with mantle-normalized ratios of (La/Sm)PM <1 to >4, (Zr/Y)PM <1 to >5, (La/Yb)PM <1 to >20 and (Nb/Th)PM significantly below 1, i.e. from values inferred for mantle-derived melts to values more typical of continental crust. By contrast, HFSE inter-element ratios (Nb/Ta ~ 16.2, Zr/Hf ~ 36.8) and initial Nd-Hf isotope values are homogeneous (εNd = 1.4 ± 0.5; tPM = 2.2 ± 0.8), yielding ~3.45 Ga isochron ages which are consistent with known emplacement ages.

Our Nd (and Hf) isotope results are consistent with those of Jahn et al. [2] and Gruau et al. [3] and do not appear to support a significant contribution from assimilated enriched Hadean proto-crust to ~3.45 Ga basaltic magmatism. Additional modeling will help to further assess the involvement of potential crustal contaminants.


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Linking noble gas and CH$_4$ concentrations in the sediment porewater of Lake Lungern, Switzerland

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Noble gases are powerful tracers for gas transfer processes in lake sediments. They were successfully applied in the sediment of Swiss Lake Sopensee [1] to study CH$_4$ ebullition in the past. Here, we employed a newly developed method for quantitative sampling of dissolved CH$_4$ and noble gases [2] to determine both CH$_4$ and noble gas concentrations in the porewater. In order to assess the depth of active CH$_4$ production, and to investigate gas transfer processes in the lake sediment we sampled the uppermost metre of the sediments of Lake Lungern, a Swiss hydropower reservoir. This lake is characterised by lake level variations and the formation of CH$_4$ bubbles in the sediment due to super saturation of dissolved gases in the porewater.

Using the new sampling method, we observed CH$_4$ concentrations exceeding the in-situ saturation concentration. Compared to the overlying water body, the noble-gas concentration in the sediment porewater showed a depletion of the lighter, more volatile gases relative to the heavier, more soluble gases. This elemental fractionation indicates stripping of noble gases into the CH$_4$ bubbles in the sediment due to super saturation of dissolved gases in the porewater.

In order to study the gas transfer processes in the lake sediment, we sampled the uppermost metre of the sediments of Lake Lungern, a Swiss hydropower reservoir. This lake is characterised by lake level variations and the formation of CH$_4$ bubbles in the sediment due to super saturation of dissolved gases in the porewater.

Using the new sampling method, we observed CH$_4$ concentrations exceeding the in-situ saturation concentration. Compared to the overlying water body, the noble-gas concentration in the sediment porewater showed a depletion of the lighter, more volatile gases relative to the heavier, more soluble gases. This elemental fractionation indicates stripping of noble gases into the CH$_4$ bubbles in the sediment. In addition, the absolute noble gas concentrations in the sediment porewater indicate an air excess relative to the concentrations in the overlying water body. We attribute this to the formation of excess air resulting from the dissolution of air bubbles entrapped in the sediment when the lake level falls below the depth of our sampling site. Linking CH$_4$ and noble gas concentrations in the sediment porewater therefore allows assessing importance of the physical transport processes related to CH$_4$ emission from the sediments into the water body of the Lake Lungern.


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