Intra-transform magmatism; Melt migration and two-component mantle

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Oceanic intra-transform magmatism is not supported by long-lived magma chambers or along-axis transport of melt from other parts of the spreading system, thus providing well-defined locations of melt delivery and crustal formation. Intra-transform basalts therefore represent pre-aggregated melts and their compositions provide insight into models of melt generation and transport processes beneath mid-ocean ridges. The Quebrada/Discovery/Gofar (QDG) transform fault system offsets the fast-slipping East Pacific Rise (3°-5°S) by approximately 400km and is composed of 8 active intra-transform spreading centers ranging in length from 5 to 70 km. Forty-seven dredges of young intra-transform basalts were collected and geochemically characterized from this area.

QDG basalts exhibit varying degrees of differentiation, which correlate with the estimates of crustal thickness of each ridge segment derived from gravity models. The incompatible trace element ratios (e.g. Th/La) of these lavas range significantly from depleted to enriched compositions at similar MgO content, and the level of enrichment correlates well with indicators of depth of melt segregation (e.g. Sm/Yb). Overall, the chemical variation of these basalts is greater than that previously found in fracture zones (such as Siqueiros and Garrett FZ) and is similar to the compositional range defined by northern EPR seamounts.

A simple geochemical model reproducing the trace and isotopic data of QDG basalts suggest that melting of a two-mantle component and the effect of melt migration can easily explain the compositional range observed at mid-ocean ridges.

Arsenic in siliceous deposits formed from geothermal water

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Arsenic in geothermal power plants

Geothermal water, which discharges from deep underground, contains various harmful elements since it is volcanic origin. Especially, arsenic (As) concentration of geothermal water is outstanding and is generally several ppm. Therefore, the geothermal water after water/vapor separation for electric generation has been returned into deep underground again through re-injection wells at geothermal power plants. On the other hand, siliceous deposits, which are formed from geothermal waters, have been discharged into environment as industrial wastes. However, they are possible to take up As from geothermal water during the formation. Whereas, the uptake mechanism of As by siliceous deposits formed from geothermal water and its chemical state have never been investigated. In this study, the uptake mechanism of As by siliceous deposits in geothermal water at a geothermal power plant and change in the chemical state of As during the formation of siliceous deposits was investigated.

Results and Discussion

From the correlation analysis between elements in siliceous deposits formed from geothermal water at the Hatchobaru geothermal power plant, Japan and rare earth element pattern of the geothermal water, As can be concluded to be taken up by coprecipitation with hydrous iron (III) oxide. Although the siliceous deposits were formed from oxidizing geothermal water, the inside of the deposits was considered to be in reducing environment because of the conversion of hydrous iron (III) oxide to pyrite. No As was contained in the pyrite. Due to the conversion, the As may immigrate from Fe phase to silicate phase based on the result of chemical leaching treatment.
Mineralogy of speleothems in the Khas-e-Tarash Cave, northeast Isfahan, Iran

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New Method and Discussion

Speleothems are a kind of secondary minerals that form in caves. These deposits have different landscapes and mineralogy properties. In this research, the Khas-e-Tarash Cave, which is in the northeast of Isfahan, central Iran, is studied and introduced for the first time. We considered 59 stations in the cave and all of 19 speleothem samples are studied. Results of the scanning electron microscope (SEM) and X-ray powder diffraction (XRD) analyses indicate that calcite \((\text{CaCO}_3)\), aragonite \((\text{CaCO}_3)\) and the other minerals are gypsum \((\text{CaSO}_4\cdot2\text{H}_2\text{O})\), thenardite, halite and in some cases quartz minerals are formed by groundwater along joints, fractures and main cave saloons (A sample of XRD figure 1).

Figure 1: X-ray powder diffraction pattern of one sample, it shows that minerals are sulfates with clay minerals.

A new method, in AAS analyses, stransium measured and the results show some samples only consist of carbonate. This survey shows that carbonate speleothems have calcite and aragonite. The evaporite minerals consist of different shapes in gypsum minerals (very fine to coarse), halite and thenardite. Silicon observed is in some cave deposits that indicate a change in groundwater composition. Later erosion and solution by groundwater have deformed old speleothems.

These minerals contain from four different chemicals classes; carbonates, sulfates, halides and silicates that sometimes stained by clay minerals and Iron oxide.

The tectonic setting where faults allowed the ascension of hydrothermal solutions and the deposition of the quartz minerals.

These minerals precipitated in low-temperature vadose solutions (calcite, aragonite, hydromagnesite, etc.).

Preliminary results of magnetic fabric of the Gole-zard pluton, Aligoodars, Iran

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A magnetic fabric study was performed on the Gole-zard pluton in an attempt to understand its emplacement history. Gole-zard granitoidic body (~20 km²) is located in the north of Aligoodarz cities (SW of Iran), Sanandaj-Sirjan structural zone and ranges compositionally from granodiorite-granite to leucogranite. The pluton intruded in middle Jurassic metapelitic rocks and base on age determinations on the Sanandaj-Sirjan magmatic and metamorphic belt, it belongs to middle Jurassic (155-175 Ma). The presence of metapelitic and metasandstone enclaves, silica veins xenoliths with metamorphic origin, xenocrysts of andalusite and garnet confirm its S-type character. According to the geochemistry data, the rocks are peryluminous and calc-alkaline.

The mean magnetic susceptibility obtained from different rock groups are as follows: granodiorites \((225 \, \mu\text{SI})\), leucogranites \((56 \, \mu\text{SI})\), and chloritized granodiorites \((510 \, \mu\text{SI})\). Obtained results characterize that granodiorites (the main part of this pluton) associated with leucogranites are accommodate with S-type granite. Km values increase in proportion to abundance of biotite and ilmenite. Km values reduce from granodiorites to leucogranites and finally tourmaline bearing leucogranites. In spite of distribution of magmatic microstructures in all parts of pluton, the eastern part show some evidences of solid state deformation microstructures including alteration of biotite to muscovite, chlorite and hematite; kinked biotite; mechanical twining in plagioclase and chessboard pattern in quartz.

Anisotropy percentage \((P\%)\) and shape parameter of magnetic ellipsoid \((T\) values vary from 1 to 3, and -0.43 to, in respectively. With respect to variation of \((P\)) and \((T\) values and microstructural evidences, eastern parts of Gole-Zard g pluton have undergone more intensive deformation.
Magmatic evolution of Azna-Aligoudarz granitoidic plutons, SW of Iran: A typical example of S type granitization

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Darreh Bagh, Gol-e Zard and Azna plutons located in the Sanandaj- Sirjan zone, SW Iran. Based on mineralogy and geochemistry, these plutons are S -type granites with compositional range from granodiorite to leucogranite. Special characteristics of them are: presence of andalusitic xenocrysts, andalusite bearing metapelitic enclaves, xenolithic silica (quartz fragments), metasandstone and micaschistic enclaves, microgabbroic (or basaltic) dikes cutting Gol- e- Zard granitoid pluton. Field relationships show evidences for intrusion of basic – intermediats magmas (with gabbro to diorite compositions) into metapletic rocks (slate, phyllite, micaschiste and garnet micaschist) and resulted in contact metamorphism and converting the metapletic rocks to cordierite hornfels, andalusite hornfels and silimanite hornfels. With increasing temperature, migmatites appeared and produced granitoidic melt. Then, they ascended to higher levels in the upper crust. More differentiated members including pegmatite and leucogranites dikes, tourmaline veins and veinlets, and tourmalinites cut granitic- granodioritic rocks. Since these plutons are believed that belong to the tectonomagmatic events in Sanandaj-Sirjan zone and subduction of neothethys, basic – inter mediate magmas derived from melting oceanic slab undergoing or mantle source. In conclusion, it seems interval time between emplacement of basic – intermediate and felsic magmas is not so long.

Microstructural and AMS investigation of Darre Bagh granitoidic pluton (SW Iran)

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Darre Bagh granitoidic pluton (60 km²) is located in the north of Azna-Aligoodarz cities (SW Iran) and in Sanandaj-Sirjan structural zone. The pluton intruded in middle Jurassic metapelitic rocks and base on age determinations on the Sanandaj-Sirjan magmatic and metamorphic belt, its age is obtained 169-170 Ma. This pluton compositionally ranges from granodiorite, granite to leucogranite. Small tourmaline bearing pegmatites are also observed in some parts of the studied pluton. The presence of metapletic and metasandstone enclaves, xenolithes of silica veins with metamorphic origin, xenocrysts of andalusite and garnet, ubiquitous presence of biotite association with metapletic host rocks confirm peraluminous and S-type granite nature of the studied rocks.

This pluton has been examined by anisotropy of magnetic susceptibility method (AMS) for the first time. Based on our investigations in 86 stations (249 cores and 854 fragments), average of measured mean magnetic susceptibility (Km) for different rock groups are as follows: granodiorites (Km=248.5 µSI), leucogranites (Km=52.6 µSI), migmatites (Km=415.1 µSI) and enclaves (Km=391.3 µSI). Obtained Km values (in Geomagnetic Lab of Shahrood University of Technology) indicate that main part of this granitoidic pluton (biotite bearing granodiorites) belong to paramagnetic granitoids (0<Km<500 µSI). Mean magnetic susceptibility is decreased from granodiorites to leucogranites which accommodates with decrease of ferromagnesian minerals (in particular biotite). The other magnetic behavior carriers are sphene, ilmenite and tourmaline. Therefore, there is a direct and logical relationship between lithological and mineralogical compositions and Km values. Hence, we can use Km values with reliable, for interpretations of compositional evolutions of granitoidic rocks.

Submagmatic and high to medium temperature subsolidus microstructures are visible in most of the thin sections prepared from core samples. The most interesting features of deformation in Darre Bagh pluton are as follow: subgraining of quartz, plagioclase, orthoclase and biotite; mechanical twinning in plagioclase; producing kinked biotite, chessboard pattern and undulose extinction in quartz, plagioclase and orthoclase; myrmekite rim along the margin of plagioclase; alteration of biotite to muscovite and chlorite and neoformation of secondary sphene and finally sericitization of orthoclase and plagioclase. The percentage of anisotropy (P%) values vary from 2 to 10 and show positive correlation with degree of deformation. Shape parameter of magnetic ellipsoid (T) values varies from 0.78 to -0.58 and most of magnetic ellipsoids are oblate.
Deciphering the significance of hopanoids in the marine geologic record

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Hopanoids are pentacyclic triterpenoids produced by some bacteria that have been dubbed bacterial ‘sterol surrogates.’ Hopanoids have been broadly applied in the marine sedimentary record as taxonomic markers for certain groups of bacteria and their associated biogeochemical processes. However, our ability to rigorously interpret the significance of hopanoids in the geologic record has been greatly limited by a dearth of knowledge surrounding the sources of hopanoids in marine environments. Despite the ubiquity of hopanoids in modern and ancient marine sediments, their precise provenance in the modern oceans is largely unknown. In this study, we present a survey of bacteriohopanepolyols (BHPs) in a diverse selection of marine and proximal marine environments. Our work establishes the presence and ubiquity of hopanoids in the oceans, and provides fresh insight on the environmental sources and biogeochemical significance of hopanoids in marine sediments. We observe pronounced heterogeneity in the spatial and temporal distribution of BHPs, indicating the potential for the application of hopanoids as biomarkers for biological processes in the upper ocean and as tracers for organic matter input to sediments. In particular, BHPs appear to be relatively abundant and structurally diverse in low oxygen and oligotrophic environments and in particulate organic matter (OM) transported by rivers from terrestrial environments. Given the rich structural diversity of BHPs in terrigenous OM, interpretations of the sedimentary record of hopanoids in coastal marine settings must resolve inputs from marine pelagic and terrestrial sources. Furthermore, BHPs produced in suboxic and anoxic pelagic environments likely represent an important input to the sedimentary hopanoid inventory in upwelling environments and anoxic marine basins.

The Shatsky Rise supervolcano

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Oceanic plateaus are igneous mountains constructed by massive eruptions of basalt and related igneous rocks. Because they are hidden beneath remote parts of the oceans, the structure and evolution of these mountains are poorly known. Shatsky Rise, in the northwest Pacific, is an oceanic plateau that formed during the Late Jurassic and Early Cretaceous (145-125 Ma) near a triple junction of spreading ridges. It consists of three large volcanic massifs and a narrow volcanic ridge. It is inferred that eruptions began with the largest massif (Tamu Massif) and waned through time through the formation of the other massifs. Tamu Massif is a supervolcano, i.e. a single volcanic edifice, like a seamount, but much bigger. It has an area similar to Olympus Mons on Mars, the largest volcano in the solar system. Geophysical data show that Tamu Massif has a central summit, and a shape that is symmetric across its axis. Volcanic slopes are low, implying long, low viscosity lava flows. A seismic profile across the volcano axis shows lava flows flowed outward from the axis. Seismic profiles in some spots over these axes show normal faulting that imply volcanic rift zones. Coring on Integrated Ocean Drilling Program (IODP) Expedition 324 recovered basalt flows of two types: pillows and massive flows. Pillows are indicative of normal seamount volcanism at low effusion rates whereas the massive flows imply high volume lava flows with high effusion rates. Massive flows are typical of continental flood basalts and are also found on other large plateaus. On Shatsky Rise, thick massive flows are found on Tamu Massif, whereas pillows and thin massive flows characterize the other massifs. This trend supports the idea that Tamu Massif was formed by an initial massive eruptive event and afterwards volcanism waned as other massifs were erupted. Shallow water fossils and depth-diagnostic rocks and sediments indicate that the summits of Shatsky Rise massifs were near sea level at the time of formation. Expedition 324 cores recovered hyalo-clastites and volcanic sedimentary rocks implying that explosive volcanism was significant near the volcano summit. Heavy alteration of rocks from the shallower parts of the volcanoes suggests that warm fluids flowed through the volcano summit rocks. In sum, the structure and evolution of Tamu Massif appears much like that of a typical seamount, except that it is much bigger and was built by correspondingly larger and widespread eruptions.
Environmental impacts of abandoned VMS deposits: An example case from NE Turkey

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The eastern Black Sea Region (NE Turkey) is well known for massive sulphide deposits. The abandoned mines near Espiye (Giresun, NE Turkey) are characterised by widespread slag disposed of along valleys into streams and tributaries causing serious environmental pollution. This study presents physical and chemical features of stream and spring waters and their degrees of pollution based on a sampling programme in August, 2010.

In the Ficklin diagram [1], three groups of samples collected from highly polluted mine effluent (along Acısu tributary), areas of slag disposal sites and upstream from the mine effects plot in high acid-extreme metal and high acid-high metal fields, acid-high metal field and near neutral-low metal field, respectively. The water samples from the zones near the effluent are highly polluted and contain extremely anomalous values of S, Fe, Cu, Zn, As, Cd, Pb with values as high as 1375, 1130.12, 71.37, 53.08, 2.15, 0.21, 0.1 mg/L, respectively. After about a km downstream from the effluent, these values are diluted to a great extent, especially for Pb, Fe and As. Elevated levels of other elements continue further. In contrast, the waters of tributaries draining slag piles have much lower levels of heavy metals, with some elements such as As and Fe having undetectable concentrations.

In the Acısu tributary, SO₄ is highly enriched (up to 5410 mg/L) due to microbial oxidation of sulfides. 16S rRNA analyses on water samples from this area indicates presence of Acidithiobacillus ferrooxidans at 98% precision.

The sediments are in compliance with this, and are enriched in As, Mo, Pb, Cu, Cd, Zn, Hg and Fe based on geoaccumulation (I geo) values [2]. These values are significantly high and denote heavy contamination in stream sediments along the Acısu tributary. The sediments with the surface waters are potentially hazardous to the environment adjacent to the abandoned Karaerik mine and thus are in need of remediation.


Prograde P-T path of a ~3.2 Ga tectonometamorphic event from Assegaai greenstone belt, SE Kaapvaal Craton

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P-T pseudosections are being used extensively in modern petrological studies not only to determine the P-T conditions of peak metamorphism but to establish how these conditions have been achieved, i.e. the tectonic scenario related to such processes [1]. In the present study we have used P-T pseudosection to determine the prograde P-T path from amphibolite facies garnet-staurolite-chlorite-albite-quartz-ilmenite-bearing pelitic schist from the Archaean Assegaai greenstone belt, SE Kaapvaal craton.

The pelitic schist forms part of a supracrustal sequence consisting of amphibolite, BIF, talc-tremolite schist, quartzite and calc-silicate. Within the metapelite, garnet and staurolite form the peak metamorphic assemblage and are replaced by chlorite. Absence of inclusions of any prograde mineral within garnet and staurolite porphyroblasts hinders application of any conventional thermobarometry to determine the prograde and peak metamorphic conditions.

Pseudosection analysis reveals that the garnet and staurolite assemblage was formed along a clockwise P-T path by breakdown of chloritoid: Fe-Chloritoid = almandine + Fe-Staurolite, a common reaction in pelitic rocks under amphibolite-facies conditions. Peak P-T conditions are estimated at ~8 kbar, 600-625°C. Chlorite and albite were formed during post-peak decompression and cooling by breakdown of garnet-staurolite and paragonite, respectively.

Zircon crystalisation ages (207Pb/206Pb, SHRIMP) obtained from syntectonic quartzofeldspathic veins derived from partial melting reveal that peak metamorphism occurred ~3.18 Ga. The clockwise P-T path from the metapelite indicates a collisional tectonic event similar to that reported from other greenstone belts of SE Kaapvaal craton [2, 3], that marked stabilisation of the craton at ~3.2 Ga.

Geochemical and age of collision-related volcanism following the closure of the Neotethys Ocean (Lesser Caucasus, Armenia)

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In the Lesser Caucasus in Armenia, collision of the South-Armenian Block (SAB) and Eurasia started during the Paleocene and was forming the Amasia-Sevan-Akera Suture zone (ASASZ). Magmatism covering the suture zone occurred during this collision and is particularly widespread since Middle Eocene. Moreover magmatism occurred after the Arabian plate collision with Eurasia since Miocene. In order to add constraints to the geodynamic context of these magmatisms, an extensive geochemical study (major & trace elements, isotopes) and geochronological study has been developed on 19 magmatic rocks. Only scarce geochemical and geochronological data are available on the Middle to Late Eocene volcanism which is associated to calc-alkaline to alkaline mildly alkaline compositions.

12 zircon grains extracted from a rhyodacite sample from SAB have been dated by U-Pb laser ICP-MS ablation which gives a well-concordant middle Miocene age of 14.6±0.2 My.

The rocks are overall characterized by enrichment in large ion lithophile elements (LILE) and show significant enrichment in light rare earth elements (LREE) compared to heavy rare earth elements (HREE) with (La/Sm)n evolving from 2.2-7.3 and (La/Yb)n ratios ranging between 2.5 and 16 and up to 47 for the rhyodacite. Extended rock-patterns of the ASASZ samples show positive anomalies in Pb, Sr, Ba associated to negative Nb and Ta spikes typical of subduction or back-arc environments. A more continental character is evidenced for trachyandesites of late Eocene and rhyodacite of middle Miocene ages due to possible slab retreat, a break off and continental crust heating by rising of the asthenospheric mantle (Sosson et al. 2010).


Geochemical reactivity of submarine tailings from the Batu Hijau Mine

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Batu Hijau is an open pit mine, located in south-western Sumbawa, Indonesia, with economic mineral recovery achieved through sulphide flotation and copper-gold concentrate production. Mine tailings are discharged to Senunu Submarine Canyon via an engineered deep sea tailings placement (DSTP) system. The tailings pipeline terminus is at a water depth of 125 meters from which solid tailings flow down the canyon slope to settle at depths approximately 2,000-4,000 meters. The ore processed at Batu Hijau is categorized as fresh ore from the pit, medium and low grade, with the majority of the latter two reporting to the ore stockpile where they may be stored for several years prior to processing. The fresh ore tailings contain primarily unreactive gangue material and residual sulphides. Extensive global scientific research as well as site-specific data has conclusively demonstrated that fresh sulphidic tailings are geochemically stable when permanently stored under a water cover due to greatly reduced sulphide oxidation rates arising from the limited availability and diffusibility of oxygen in water as compared to air. Conversely, the stockpiled ore is exposed to oxygen and rain prior to processing resulting in the partial oxidation of precursor sulphides and formation of secondary weathering and oxidation products. Disposal of oxidized minerals within the tailings to the marine environment may result in the reductive dissolution of oxide and oxyhydroxide phases potentially resulting in an increase in mobility of metals to overlying seawater. Field experiments were conducted in 2010 to assess the geochemical reactivity of tailings derived from processing of fresh and partially oxidized ore in the marine environment. Redox sensitive parameters and trace metals in tailings porewater and the overlying seawater were measured at high spatial resolution through the use of dialysis arrays (peepers). Mobility of contaminants of concern and the geochemical reactions governing the reactivity of submarine tailings were assessed from the porewater geochemical data. Copper efflux rates of less than 0.7 µg/cm²/year were calculated for both types of tailings from the porewater chemical profiles.
Studying soft X-ray absorption edges under extreme conditions

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The study of absorption edges has proven a powerful tool to investigate the local and electronic structure of materials. [1] Absorption edges of medium or high Z elements can be accessed using X-ray absorption spectroscopy even under extreme conditions. However, the in situ study of low Z elements absorption edges under extreme conditions, i.e. high temperature and high pressure, is not feasible using soft X-rays or electrons as probe. Here, non-resonant X-ray Raman scattering (XRS) as an energy loss technique enables one to choose the energy of the primary X-ray beam freely and thus gives access to shallow absorption edges even in highly absorbing sample environments such as diamond anvil cells. [2]

In this contribution we enlighten the approach of XRS as a tool to access shallow absorption edges under extreme conditions and present first results of in situ studies of solids and liquids under high temperature and high-pressure conditions. In particular, the Ba N45- and Si L23-edges of the silicon clathrate Ba8Si46 was studied at pressures up to 19.4 GPa. Data of the Si and Al L23-edges of hydrous sodium silicate and aluminosilicate glasses are presented and compared to the first in situ high pressure - high temperature data on hydrous silicate melts. In addition, the O K-edge of supercritical water was studied to acquire insights into its local structure. Finally, the potential of XRS for determining the Fe oxidation state from the Fe L and/or M-edge is explored.


An oxygen window for early Ediacaran animal life

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Complex multicellular organisms including early metazoans appeared in the Ediacaran Period shortly after the termination of the late Cryogenian (Marinoan) glaciation about 635 million years (Myr) ago. Given that metazoans have high respiratory demands, it has been speculated that the termination of the Marinoan glaciation, the rise of oxygen, and evolution of complex life forms were casually linked. Previously published geochemical data, however, suggest that a major increase in the extent of ocean oxygenation did not happen until the middle Ediacaran Period, 50 Myr after the first appearance of animal fossils. This later oxygenation is arguably linked to the termination of a much less severe Gaskiers glaciation around 580 Myr ago. Here we report new geochemical data from early Ediacaran (ca. 632 Myr ago) organic-rich black shales of the basal Doushantuo Formation in South China. Iron speciation and sulfur isotope data indicate pervasive deep-water euxinia (anoxic and sulphidic) and an increase in the marine sulphate reservoir from the oxidative weathering of crustal sulphides. High molybdenum (Mo) and vanadium (V) enrichments (Mo: 120 parts per million [ppm] and V: 6000 ppm) in these shales record an increase in the oceanic Mo and V reservoirs and hence point toward a significant post-glacial oxygenation event. Our data provide evidence for co-evolution of marine redox conditions and early animals in the immediate aftermath of the Marinoan glaciation.

Inventory of particulate matter from all possible major sources for air quality forecasting during Commonwealth Games 2010 in Mega City Delhi

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Mega city Delhi, is facing large urban agglomerations which is one of the largest urban concentrations in South Asia and a fast growing economic center. Adverse impact of air pollution on human health, welfare and ecosystem is a key environmental problem in Indian mega cities as well as worldwide. High resolution emission inventory (EI) is one of the important and essential critical input to air quality modeling and should be as latest as possible. As part of the System of Air quality Forecasting and Research (SAFAR) project developed for air quality forecasting during the Commonwealth Games (CWG) – 2010, a high resolution emission inventory of PM10 and PM2.5 have been developed for the mega city Delhi for the year 2010. The comprehensive inventory involves detailed activity data and developed for a domain of 70kmx65km with a 1.67kmx1.67km resolution covering Delhi and surrounding region using Geographical Information System (GIS) based statistical modeling. Developed high resolution EIs of PM10 and PM2.5 for the air quality forecasting includes the technological specific activity data for different sectors were collected from primary source through one year field campaign as well as from secondary source which is first of its kind of attempt have been made in this work not only to fill the gap but also improve the understanding, uncertainty and accuracy of inventory. It has been found that total emission of PM10 and PM2.5 over the study area is found to be 236 Gg/yr (as shown in Fig.1) and 94 Gg/yr respectively. The contribution of windblown road dust is found to be as high as 131 Gg/yr for PM10 which is unusual. The relative contributions of different sectors are discussed with possible target for mitigation.

![Figure 1: PM10 emission from different sources over Mega city Delhi.](image)

Positive Ce anomalies and U-enrichment in Archean volcanics: Implications for oxygenated oceans

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Inference of reducing conditions in the Archean are mostly based on local evidence such as paleosols. Accordingly, new data from the scale of ocean basins is presented. Boninites in unweathered volcanic sequences of the 2.7 Ga Gadwal greenstone terrane, Dharwar craton, India, record systematic positive anomalies of U relative to Th on primitive mantle normalised diagrams, where Th/U spans 0.9-2.1 versus ~ 4 in tholeiitic basalts [1]. Such patterns are present in Phanerozoic forearc boninites where oxygenated fluids are released from the subducting slab into forearc mantle wedge. Adakites, interbedded with pillow basalts, of the ~ 2.6 Ga Hutti greenstone terrane, Dharwar craton, record Ce/Ce* ~ 1.2-1.3 with Th/U ratios <4 consistent with additions of Ce and Th from oxygenated ocean waters. Systematic positive anomalies of Ce, where Ce/Ce* spans 2.1 to 11.4, are present in basaltic and rhyolitic of a 2.9 Ga submarine volcanic sequence, Murchison Province, Western Australia; these are true Ce anomalies as Pr/Pr*<1. These extreme anomalies are attributed to a stratified ocean, with oxygenated surface waters but reduced bottom waters, in which Ce 4+ was sequestered, then co-precipitated with Fe-, Mn-oxides and hydroxides distal to a submarine hydrothermal system that generated the Golden Grove Zn-Cu VMS deposit. Archean BIF of the Dharwar craton preserve negative Ce anomalies, complementary to the positive anomalies in volcanic sequences. Collectively, these observations, at the scale of ocean basins, preserve the record of an oxygenated marine environment ~ 400 Ma before the so-called great oxidation event (GOE) at ~ 2.4 Ga.

Spectroscopic estimation of SiO$_2$ for characterizing clays in the Brahmaputra river sediment

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We report here the characterization of sediments from the Brahmaputra river. The samples were collected along the stretch of the Brahmaputra river channel. Analysis of the sediment is presented with the help of FTIR and XRF spectroscopic methods. Clay mineral analyses provide evidence for diagenesis. The maturity index of sediment and extinction coefficient of SiO$_2$ inclusion reflects the nature of erosion quality of the river. The major constituents of the samples are silica, alumina, which confirms the chemical analysis of clay. The LOI was determined at 800°C. The relatively large difference in the LOI values between 9.87 wt % and 22.21 wt % indicates that greater loss on ignition took place during the calcination step. This is largely due to the giving off of structural hydroxyl water and volatile organic components. The samples showed SiO$_2$ contents between 34.77 and 56.41 wt%. The grain size of the sediment samples are measured from the SiO$_2$/Al$_2$O$_3$ (wt %) ratio. The maturity index is invalidating with grain size of the samples, which indicate that the maturity increases with the decrease of quartz content and grain size. The correlation of the K$_2$O, TiO$_2$, Na$_2$O and MgO with Al$_2$O$_3$ indicate that these compounds of the sediment samples are completely associated with detrital phases of erosion process of the river. The region 400-800 cm$^{-1}$ represents generally the bands assigned to the O-Si-O and O-Al-O stretching region. The region 800-2000 cm$^{-1}$ contains the Si-O and Al-O stretching modes and the region 2600-4000 cm$^{-1}$ represents the OH stretching modes. In the O-Si-O and O-Al-O bending region of the infrared spectra of the studied samples are complex and there is a significant overlap between the quartz and kaolinite bands. The deposition of kaolinite in the sediment samples of the different stages of the river track can be differentiated on the basis of its quartz content. Comparison between the maturity index and extinction coefficient of the sediment samples shows a marked increase of SiO$_2$ content.

Spectroscopic characterization of olivine due to Fe/Mg in Dergaon H5 chondrite

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The effect of the Fe and Mg ratio of olivine group [(Mg$_{n}$Fe$_{2-n}$)SiO$_4$] in the Dergaon H5 chondrite has been investigated by Fourier Transform infrared (FTIR) and X-ray florescence (XRF) analysis. The change of peak positions of the SiO$_4$ tetrahedra in the stretching region have been observed with the Fe, Mg contents. The special interest is given in systematic band shifts in forsterite- fayalite series. The SiO4 tetrahedra are isolated in the structure and linked by cations Fe$^{2+}$ or Mg$^{2+}$ in octahedral positions. The cation positions in the structure can be filled with iron and magnesium in all possible ratios and sometimes it is occupied by Ca$^{2+}$ or Mn$^{2+}$. The iron and magnesium (Fe/Mg) ratio in olivine is expressed as the forsterite content, and is calculated from the atomic percentage of Fe and Mg in the measurements. The variation of forsterite and fayalite compositions are Fo 66-89 and Fa 10-33 mol % respectively. The plot of Fo and Fa against the corresponds wavenumbers for the bands 1to5 of olivine group of the meteorite sample shows a linear variation for Fo and Fa in a different direction. The factors responsible for the frequency decrease of the absorption bands with an increase in iron may be the effects of replacing an ion of smaller radius (Mg$^{2+}$ of radius 0.66Å) with a larger one (Fe$^{2+}$ of radius 0.74 Å). The infrared bands in the 10mm region of the meteorite sample exhibits good agreement with the XRF results. In the 600 - 4000 cm$^{-1}$ region, the pyroxene shows a ‘V’ shape in the infrared spectra. This band shape depends upon the Mg/Fe ratio in the sample.
Spectroscopic studies of silicate minerals from North-Eastern India

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The samples we reported here are collected from North-Eastern region of India in their almost pure form of quartz crystal and silicates. Here an overview of the basic morphological, physico-chemical and crystallographic characteristics of the silicates is given. Particular emphasis is given to make a catalogue of silicates on the basis of structural classifications. The colour of the quartz crystal of these locations indicates the inclusion of the trace elements present in the host rocks. The compositional and structural studies were carried out at room temperature by using X-ray fluorescence (XRF), electron microprobe (EPMA) analyses and Fourier transform infrared (FTIR) spectroscopic techniques. Differential thermal analysis (DTA) and thermo gravimetric studies were also performed. The results of the compositional analysis of the samples are comparable to the standard literature. The compositional analysis of the samples exhibits that the major trace elements are Fe, Al, Ca and Mg. The optical properties are compared with the standard literature and the results are found to be satisfactory. An attempt to identify the minerals using the FTIR spectroscopy and to classify them according to their structural characteristics is performed. The crystallinity investigation throws light on the dependency on temperature and pressure during formation. The purity and distributions of the samples can also helps on the economic and industrial values of the silicates of the study region.

A rough idea about the silicate minerals of the study area can be lead from this investigation. Since silicates are known as rock forming mineral, one can have a fairly good idea about the rocks found in these areas.

Complexation of Eu³⁺ with humic substances studied by time-resolved laser fluorescence spectroscopy and parallel factor analysis

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Humic substances (HS) are heterogeneous and ill-defined organic nanoparticles widely found in soil and aqueous environments. HS are known as effective complexants for inorganic and organic contaminants, mediating their migration through geosphere. Although many researches have been devoted to study binding of metal ions to HS mostly in terms of macroscopic binding amounts, detailed information on the binding processes are still limited, because of the heterogeneity and variety of HS from different origins. In this research, we investigated the binding of Eu³⁺ to various HS by time-resolved laser fluorescence spectroscopy (TRLFS) hyphnated with parallel factor analysis (PARAFAC). TRLFS is an analytical technique sensitive to physico-chemical forms of a target fluorescent metal ion, which can be further reinforced by combining with a powerful multivariate data analysis, PARARAC [1].

Binding of Eu³⁺ to HS purchased from the International and Japanese Humic Substances Societies was examined by TRLFS as a function of pH. A series of TRLFS data obtained for a certain HS were processed by PARAFAC to determine the number, spectra, decays and relative concentrations of factors. Except for one HS, three factors were necessary and enough to describe the variations in the data sets. These factors were distinctive with each other and could correspond to different Eu³⁺ species bound to HS. Each of the factors has some similarity among different HS, suggesting the presence of similar binding environments in different HS. It was further revealed that there were systematic trends between the spectra, decays and concentrations of the factors and the physical and chemical properties of HS. The observed trends will be used to deduce the characteristics of the different binding environments for Eu³⁺ in HS.

Viscosity measurements of FeO-rich silicate melts and its implication for the lunar crust formation
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The anorthite crust of the Moon has been thought to be the product of large-scale differentiation in the cooling lunar magma ocean, and the bulk composition of the Moon has been estimated to be richer in FeO than the bulk silicate Earth (e.g. [1]). The FeO content is a critical parameter for density and viscosity of silicate melt, and precise determination of those parameters is important for quantitative evaluation of the lunar crust. Contrary to the density, viscosity of silicate melts show complicated dependence on pressure and composition. Hence, experimental determination of viscosity of FeO-rich silicate melts is important. We have carried out viscosity measurements with the falling sphere method for silicate melts suitable for the lunar magma ocean.

The starting materials are glasses with three different compositions, which are fractionated in terms of mantle minerals to the first appearance of anorthite from the bulk silicate Earth with FeO-enrichment with various degrees.

Figure 1: Viscosity of silicate melts responsible for differentiation of the Moon.

The results are shown in Figure 1, which shows weak (or slightly negative) dependence of viscosity on pressure and clear negative dependence on the FeO contents.

Figure 1 suggests little pressure dependence of viscosity for the lunar magma ocean melt at least to P>1GPa (~ 100km). The little or weak negative pressure dependence of the melt of the magma ocean in addition to high density due to high FeO contents result in effective flotation of anorthite, that is, effective formation of the anorthite crust. Our quantitative model predicts that the initial FeO content of the Moon that finally generated the anorthosite crust with the thickness of 45km was 10 - 13 wt%, which is more than the bulk silicate Earth.


Behavior of biological and terrigenous elements during the late Cenozoic in the Bering Sea: Paleoceanographic constraints of the IODP Exp. 323 sediments by high resolution non-destructive TATSCAN scanning
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Continuous marine sediment cores during 5 myrs in the Bowers Ridge (Sites U1340 and U1341) and continental slope of the Aleutian Basin (Sites U1341, U1343, and U1344) of the Bering sea obtained by the IODP expedition 323 in 2009. Age models of the drilled cores are constructed using oxygen isotope stratigraphy, bio- and magneto-stratigraphy with astronomical calibration of non-destructive XRF core measurements (TATSCAN-F2). Estimated sedimentation rates during interglacials are two to three times higher than that of glacials.

Marine primary productivity, Si/Al ratio measured using TATSCAN-F2 representing biogenic silica content, exhibits large glacial-interglacial cycles during the Plio-Pleistocene. and. The productivity is relatively high, similar to that of today’s ‘green-belt’, during the interglacial periods with increasing glacial-interglacial variability after NHG, and even larger amplitude variations during last 500 krys. Changes of biological productivity were closely related to terrigenous inputs representing by K/Al and Fe/Al ratio that those elements derived from the Alaskan large rivers during the past 5 myrs.
Geochemical studies in Piraeus port sediments, Greece

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Introduction and methodology
Piraeus port surface sediments were geochemically studied. Total metal content and metal partitioning [1] were determined by Atomic Absorption Spectrophotometry. Metal partitioning is presented as percentages in pie diagrams. The DOM aqueous extracts were characterized by fluorescence spectroscopy for distinguishing different classes of organic components. Mono dimensional spectra [2] and contour plots (EEMS) are given.

Discussion of Results
Sediments show a high metal enrichment, especially in the outer part of the central port for Fe, Pb, Zn, Cu, Cd and Sn while seawards the outer cargo terminal for Mn, Ni, Cr and Zn. In all samples there are significant easily hydrolyzed Zn, Cu and Cd components, easily available to the biota. A carbonate related contribution of Mn and Ni was found. More than half of Cu is either bound to various forms of organic matter and/or present in sulphide minerals.

DOM consists of either simple aromatic units [2, 3] (phenolic-like, hydroxyl substituted benzoic and cinnamic acid derivatives, coumarins and alkaloid-like hydroxyquinolines) or compounds such as humic- and fulvic-like moieties and protein derived materials [4].

Iron isotope composition of the Middle Eocene ooidal-oncoidal ironstones and the associated lateritic paleosols from the Bahariya Depression, Western Desert, Egypt

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The Middle Eocene ironstones of the Bahariya depression, Western Desert, Egypt are subdivided into two marine sequences. The lower ironstone sequence consists mainly of peritidal stromatolitic and ooidal-oncoidal ironstone facies that were later subjected to subsurface alteration by acidic hot groundwater. The upper ironstone sequence consists mainly of mud-ironstones. The upper surfaces of these ironstone sequences were exposed to subaerial weathering processes, along which lateritic iron ores and paleosols were formed.

Iron isotope measurements were used to differentiate between the subaerial and subsurface alteration processes affecting the original marine ironstones. The iron isotope composition of the lateritic paleosols displays low δ56Fe values of -0.15‰ to -0.85‰, while the stromatolitic and ooidal-oncoidal ironstone facies that were later subjected to subsurface alteration by acidic hot groundwater. The upper ironstone sequence consists mainly of mud-ironstones. The upper surfaces of these ironstone sequences were exposed to subaerial weathering processes, along which lateritic iron ores and paleosols were formed. Iron isotope composition of the lateritic paleosols displays low δ56Fe values of -0.15‰ to -0.85‰, while the stromatolitic and ooidal-oncoidal ironstone facies that were later subjected to subsurface alteration by acidic hot groundwater. The upper ironstone sequence consists mainly of mud-ironstones. The upper surfaces of these ironstone sequences were exposed to subaerial weathering processes, along which lateritic iron ores and paleosols were formed.

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Development of steady-state surface topography and the determination of dolomite dissolution rates

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The knowledge of the elementary mechanisms controlling the reactivity of mineral surfaces which undergo dissolution is critical to the development of rate-models that can accurately describe the processes occurring at the mineral/water interface. The correct interpretation of experimentally measured steady-state dissolution rates is affected by the duration of the experiments and by the development of a steady-state surface morphology, particularly at conditions close to equilibrium [1, 2].

Dolomite dissolution has been studied by hydrothermal atomic force microscopy (HAFM) on fresh-cleaved crystal surfaces as a function of the chemical affinity from 60 to 100 C, while a parallel series of experiments has been performed on a mineral powder of the same origin, under the same conditions, using a mixed-flow reactor.

The microscopic observations show the development of rectangular-shaped etch pits at mildly acidic pH’s and a progressive decrease of the step velocities accompanied by a concurrent rounding of the acute step morphology when a carbonate-rich solution is introduced in the AFM cell. This change required several hours to be clearly manifested and effectively slow the rates of dissolution. Depending on the previous history of the sample, the same morphological steady-state may even require a few days to be attained. The results obtained from bulk experiments confirm the inhibiting effect of both carbonate species and aqueous Ca on dissolution and indicate that this drastic decrease of the rates is the consequence of a lower etch pit density.


Biologically enhanced silicate mineral dissolution for CO2 sequestration

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During the past two centuries release rate of CO2 to atmospheric reservoir has been increased by combustion of fossil fuels [1]. The consequence of CO2 accumulation in the atmosphere is reflected as global climate change which is one of the main challenges facing humanity today [2]. CO2 fixation as carbonates has been introduced as one the most sustainable and promising mitigation methods [3]. The efficiency of this method however is mainly limited by the raw material availability (Ca or similar divalent cations) [4]. Naturally occurring alkaline silicates are rich in divalent cations and have large reservoirs on earth; however with low dissolution rate. In the present study we describe dissolution enhancement of an alkaline silicate (wollastonite) during microbial anaerobic fermentation producing organic acids. Fermentation is an intermediate step in the anaerobic digestion process, a common process used for industrial or domestic purposes to manage waste and/or to release energy. Integration of wollastonite in an anaerobic fermentation process can result in release of Ca to the solution and neutralization of the process. ICP-OES and HPLC measurements showed an increase of dissolution rate by both proton release resulted from dissociated organic acids and complexation of Ca with these organic-products. Upon subsequent degradation of the organic acids to biogas, inorganic CO2 will be sequestered as carbonate mineral. This work could provide an alternative route to reduce climate impacts from waste treatment plants.

TIMS U-Pb dating of bastnäsite, calzirtite and tantalite as a powerful tool for timing of rare-metal granites and carbonatites (Eastern Siberia)

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Complex Ti, Nb-Ta and Zr oxides, primary HFSE hosts like baddeleyite, zirconolite, perovskite, pyrochlore are well known minerals appropriated for U-Pb dating of carbonatites, phoscorites as well as granitic pegmatites of the rare-element class. We propose to extend this list with calzirtite, tazheranite and bastnäsite.

Bastnäsite ((LREE)(CO3)F) is a typomorphic mineral of siderite carbonatites from the Karasug (REE, Ba, Sr, F, Fe) deposit (Tuva Republic) Concordant U-Pb age at 118±1 Ma was obtained for bastnäsite which is in good agreement with Sm–Nd and Rb–Sr ages [1]. The minerals of this group are widespread and, in particular, represent the major economic LREE minerals in the deposits related to nontraditional carbonate complexes, as well as occur in highly alkaline pegmatites, alkaline granites and scarns.

Tazheranite (CaTiZr2O8) and calzirtite (Ca2Zr5Ti2O16) are the characteristic accessory minerals in alkalic and ultramafic complexes associated with carbonatites. A Tazheran (SW Lake Baykal) calzirtite and tazheranite yielded a Concordia U-Pb ages at 466±2 Ma and 464±2 Ma respectively which are consistent with zircon U-Pb age at 471±5 Ma [2] as well as perovskite U-Pb age at 462.8±2.5 Ma [3].

For the first time U-Pb isotopic analyses were carried out on tantalites from three suites of pegmatites in East Sayan large-scale rare-metal province. The ages of 1838±3 Ma 1824±7 Ma and 1738±5 Ma have been obtained. These data demonstrate that mineralization is just for 30-100 Ma younger than country post-collisional Sayan granites (1858±20 Ma) [4].

Our study advertises bastnäsite, calzirtite, tazheranite as well as tantalite as promising tool for U-Pb timing of mineralization related to plumaostic type rare-metal granites and some of carbonatites.

XPS analysis of corrosion products formed on mild steel surface
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Methods of investigation
Effect of an antibacterial drug, sulfacetamide (SA), on the composition of corrosion products formed on mild steel surface in 1.0 M HCl solution has been investigated using potentiodynamic polarization, electrochemical impedance spectroscopy and XPS analysis. Fig.1 shows XPS spectra.

Discussion of Results
In presence of SA, the surface layer consists of FeO (OH) rather than pure oxide [1, 2], adsorbed molecules of SA [2] and inorganic compounds (sulfides, carbonates, sulphates, nitrates) which were obtained by electrochemical decomposition of sulfacetamide [2]. More or less hypothetical compound such as schwertmannite, an iron-oxyhydroxysulfate mineral with an ideal chemical formula of Fe8O8 (OH)6(SO4)·nH2O or Fe3++16O16(SO4)12-13·10-12 H2O may be formed. It can be considered that the SA acts as an incipient ‘rust transformer’ and favors the formation of a ‘superficial closed layer’.

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Stable isotope constraints on fluid flow in the Cascadia accretionary prism: Evidence for large flow transients during recent deformation
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The Cascadia subduction zone is a site of significant earthquakes with a recurrence interval of 240 to 530 years [1]. ODP drilling near the deformation front and on Hydrate Ridge has revealed pervasive deformation, and the formation of abundant gas hydrate, and in addition carbonate cements and veins [2]. The carbonates are proxies for fluid characteristics during he most recent active deformation and perhaps extending back to 2 Ma bp. Conventional and ion microprobe isotopic studies have shown that several fault horizons preserve carbonates with δ18OVVPDB values as low as -22‰, substantially out of equilibrium with modern pore water isotopic compositions and temperature. The values can be explained by transient flow events bringing in fluids from several kilometers remote from the drill sites, with substantially different isotopic compositions and temperatures. At one of the drill sites, δ18O values are consistent with precipitation temperatures of >100°C at a depth of only 67 meters below seafloor (mbsf). Conventional and ion microprobe analyses cannot distinguish between fluid isotopic and temperature causation of the carbonate isotopic anomalies. We are planning to measure samples using the technique of clumped isotope analysis, which relies on the correlation between the prevalence of ¹³C·¹⁸O·¹⁶O isotopologues (Δ47 measurements) in carbonate with temperature during carbonate formation, to determine temperature and oxygen isotopic composition of fluids. The new data presented here will bear on our model of periodic, nonsteady-state fluid migration in the Cascadia accretionary prism. These transient flow events likely occur at time scales of less than a year, and may be related to periodic large-magnitude earthquakes. Widespread pulses of warm fluids could potentially destabilize clathrates at Hydrate Ridge and result in release of large quantities of methane into the overlying water column and atmosphere.

[1] Goldfinger et al. (in press) USGS Prof. Paper 1661-F.
Study of Naryn river (Central Asia) runoff formation by stable isotope

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Monitoring of the isotope composition ($\delta^{18}O$, $\delta^2H$) of precipitations, Naryn river and its tributaries, groundwater, and Toktogul reservoir was carried out in 2007-2009. Isotope composition of precipitations vary from $\delta^{18}O = -1.2$ and $\delta^2H = -17 \, \text{‰}$ to $\delta^{18}O = -26.5$ and $\delta^2H = -206 \, \text{‰}$ and fits the global meteoric water line. Mean seasonal composition of precipitation in summer (Jun.-Jul.-Aug.) is $\delta^{18}O = -9.5$ and $\delta^2H = -70 \, \text{‰}$; in spring (Mar.-Apr.-May) is $\delta^{18}O = -11.6$ and $\delta^2H = -83 \, \text{‰}$, in autumn (Sep.-Oct.-Nov.) is $\delta^{18}O = -11.0$ and $\delta^2H = -79 \, \text{‰}$, in winter (Dec.-Jan.-Feb.) is $\delta^{18}O = -17.3$ and $\delta^2H = -130 \, \text{‰}$.

End-member isotopic compositions varies: a) Naryn river head $\delta^{18}O = -15.2$ and $\delta^2H = -134 \, \text{‰}$ to $\delta^{18}O = -10$ and $\delta^2H = -82 \, \text{‰}$; b) middle reach of Naryn river and its tributaries $\delta^{18}O = -10.9$ and $\delta^2H = -79 \, \text{‰}$ to $\delta^{18}O = -14.5$ and $\delta^2H = -104 \, \text{‰}$; c) Toktogul reservoir $\delta^{18}O = -14.1$ and $\delta^2H = -103 \, \text{‰}$ to $\delta^{18}O = -11.8$ and $\delta^2H = -84 \, \text{‰}$; d) groundwater $\delta^{18}O = -17$ and $\delta^2H = -126 \, \text{‰}$ to $\delta^{18}O = -13$ and $\delta^2H = -94 \, \text{‰}$.

The average isotopic composition of Naryn river just before flowing into the Toktogul reservoir is $\delta^{18}O = -13.0$ and $\delta^2H = -93.2 \, \text{‰}$, and in the reservoir itself - $\delta^{18}O = -13.0$ and $\delta^2H = -94.4 \, \text{‰}$; both are close to the mean annual precipitation $\delta^{18}O = -12.8$ and $\delta^2H = -92.5 \, \text{‰}$. Consequently, there is strong averaging of precipitations in the some reservoirs, and averaging increases with runoff.

Naryn river runoff practically has no the glacier water, because of a) isotopic composition of water in rivers is weighted in summer and lighted in winter; b) water isotopic composition in the middle reaches is heavier, than in river head, where water has moreover fingerprint of cryogenic metamorphism in isotope composition; c) river water significantly differs from the isotopic composition of ice cores on the Inylchek glacier $\delta^{18}O = -16.5$ and $\delta^2H = -105 \, \text{‰}$.

In conclusion, Naryn river runoff is formed at the expense of winter and spring precipitations. Summer precipitations can be neglected, as their volume is insignificant, and at altitudes to 1600 m precipitations are completely absorbed by evaporation. Disappearance of glaciers won't render essential influence on a river Naryn runoff.

The breakup and chemical equilibration of metal diapirs in terrestrial magma oceans

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The early history of the Earth is most likely marked by at least one global magma ocean stage. During this time window, iron diapirs of various sizes delivered by differentiated impactors may have plunged through a few hundred kilometer thick silicate magma ocean. Understanding the breakup of metallic cores in such context is key to constrain the degree of metal-silicate equilibration processes.

To address this problem, I have conducted a series of numerical experiments where I follow the sinking of iron diapirs until breakup. These models include an accurate treatment of surface tension, inertial effects, stress and composition dependent viscosity. The influence of rheological properties and diapir sizes was systematically investigated. Scaling laws for the conditions of diapir breakup have been derived and are used to determine the stable size of sinking iron bodies in a silicate magma ocean.

Using these relationships I investigate the conditions and timing for metal-silicate chemical equilibration in terrestrial magma oceans.
Determination of U-Th and Pb isotope ratios in crude oil, kerogen and asphaltenes: Potential application for dating age of expulsion of crude oil from the rock source

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The Pb-Pb, U-Pb and Th-Pb methods of dating have become in geochronometers widely used to determine ages of minerals and rocks. However, there is scarce information about their application for dating hydrocarbon samples.

A simplified concept for U-Th-Pb geochronometers is proposed to estimate the expulsion age of crude oil from the source rock. Elemental isotopic ratio U/Pb and Th/Pb were determined by Q-ICPMS after sample acid digestion. Due to the matrix composition, classical anion exchange procedures used for lead isolation in inorganic samples (like sediments, minerals or rocks) can not be applied directly in crude oil, kerogens and asphaltenes samples. Therefore purification procedures were evaluated in-depth for experimental optimal conditions and the optimized method was compared with a new developed method which consists in a two purification steps: first Pb ethylation with NaBEt4 and solvent extraction followed by second separation stage in a gas chromatograph coupled to the MC-ICPMS. This new approach providing limited sample preparation is an efficient alternative to conventional geochemical procedures, with a great potential for micro geochemical samples.

Isotopic ratios results were used for dating hydrocarbon accumulation of two petroleum basin. These results were in good agreement with the theoretical model, hence, representing a new potential tool in petroleum prospection.

Root litter decomposition and stabilisation in three different soil depths related to microbial community dynamics and enzyme activity

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Subsoil horizons located below the A horizon are known to store important amounts of organic carbon characterised by high mean residence times. Microbial biomass and activity in these horizons are most probably contrasting to those of topsoil horizons and thus influence root litter degradation in different soil depths [1]. The aim of this study was to follow 13C labelled root litter degradation in three different soil depths during a three year field incubation experiment and to establish a relation to the dynamics of microbial communities analysed by DNA fingerprinting and enzyme activities.

Our results showed contrasting decomposition dynamics in top- and subsoil horizons despite similar stabilisation processes [2]. Subsoil horizons showed a lag phase during the first months of incubation, but this retard in decomposition was compensated at the end of incubation probably by slightly better abiotic conditions at depth [2].

Enzyme activities showed distinct dynamics in different soil depths. Chitinase was the only enzyme that showed similar activity in top- and subsoil horizons; all other enzyme activities were much higher in topsoil. Activity of the enzyme involved in the N-cycle was evident in subsoil only within a short period after plant litter addition.

Dynamics of microbial populations evolved with time especially in the first year of the experiment. Thereafter changes in community composition were less pronounced. Stucture of microbial communities showed a depth gradient with the lowest soil layer being most different from the other two. This was mainly related to the first six months, where fresh root litter input obviously caused drastic changes.

We conclude, that microbial biomass and activity at soil depth are more limited by lack of fresh plant litter than by physical conditions. Both parameters can rapidly be stimulated and reach topsoil level in the first few months after root litter addition. However, these changes were only transient at 90 cm depth.

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Microbial Fe(III)-reduction in highly calcareous agricultural soils

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Although iron is the fourth most abundant element in the Earth’s crust, plants may develop iron deficiency symptoms (iron chlorosis) due to low iron bioavailability. Iron chlorosis symptoms include insufficient leave chlorophyll content, poor growth and low crop yield. In particular, plants grown on calcareous soils of arid and semi-arid regions are prone to iron chlorosis because calcium carbonate buffers pH at high pH values where iron solubility is low and soil acidification strategies of diverse plant families – which would otherwise increase iron solubility and hence availability – are compromised. Agronomic practices to alleviate iron chlorosis include the application of inorganic iron fertilizers or synthetic iron chelators. Occasionally, temporary flooding of soils was shown to increase iron phytoavailability; it was speculated that microbial iron reducing activities mobilized iron during such flooding events. However, information on microorganisms with Fe(III)-reducing capabilities inhabiting calcareous soils is scant. To study flooding effects in relation to microbial activity in greater detail, we incubated soil slurries prepared from twenty-four different calcareous soils from southern Spain in the laboratory and monitored changes in iron mineralogy. The concentration of ferrous iron remained constant in control experiments with sterilized soils. In contrast, native soils produced significant amounts of ferrous iron from soil ferric minerals and the extent of ferrous iron production correlated well with native contents of dissolved organic carbon. The addition of organic acids that are typically found in root exudates further increased the production of ferrous iron. Comparative examination of soil samples suggests significant microbial mobilization of both poorly crystalline and crystalline soil iron oxides. Threshold values required for adequate iron nutrition of tolerant plants were reached in 18 slurries of native soils and 22 of the native soils that had been amended with organic acids. Microbial mechanisms that probably contributed to the mobilization of iron include respiration, fermentation and sulfur-cycle mediated reduction of soil iron minerals.

Distribution of branched tetraether lipids in a Black Sea sediment core: Insights into continental temperature evolution in Central Europe over the past 40,000 years

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The MBT/CBT proxy based on the relative distribution of branched tetraether membrane lipids found in peat bogs, soils and ancient sediments is a promising tool for past annual air temperature and soil pH estimations. The first studies support its application in marine sediments (e.g. [1, 2]). Nevertheless the uncertainties on the source of the biomarkers (producing organisms and/or possible aquatic production) and the need of new calibration datasets clearly speak for more studies.

We present the first paleo-record of branched tetraether lipids in Central Europe from a sediment core retrieved in the Black Sea, over the past 40,000 yrs BP. As the Black Sea encountered a transition from a lacustrine to a marine stage at the beginning of the Holocene period, we could explore the MBT/CBT proxy in the two realms. During the marine stage and especially during the reconnection of the Black Sea to the Mediterranean Sea, MBT/CBT-derived temperature profile seems to be biased possibly due to the major reorganization in the water column and/or the salinity shifts. However, using the MBT/CBT global lake calibration [3], the core-top yields reconstructed temperatures similar to the instrumental spring temperature in the Black Sea basin and to the present mean annual atmosphere temperature registered above the core. Whatever calibration datasets, the Holocene/LGM reconstructed temperature drop is consistent with existing paleo datasets from the area. Furthermore, the temperature profile of the last glacial period shows synchronous variations with major climatic events recorded elsewhere in the Northern Hemisphere.

**CaCO₃ polymorph growth and stabilization in water-ethanol mixtures**

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Alcohol-water mixtures can control the mode of precipitation and morphology of crystalline CaCO₃. However, these two characteristics are sensitive to experimental parameters such as concentration, calcium source, temperature, precipitation method and mixing speed. An understanding of the growth of CaCO₃ in alcohol-water mixtures is important because control of the precipitating polymorph and its morphology are two central parameters for successful biomineralization of CaCO₃.

We used a simple, homogeneous precipitation method, where we fixed temperature (24 °C) and total concentration of CaCl₂ and Na₂CO₃ (25 mM) and varied the proportion (10 and 50%) of alcohol, shaking speed, type of alcohol (ethanol, 1-propanol and 2-propanol) and reaction time (1 h to 4 m). Diffraction and imaging results show that shaking speed and alcohol concentration are the determining parameters for vaterite and aragonite stabilization. They also control vaterite morphology, which varies from cauliflower shaped aggregates to dendrites (Figure 1). We also present an equation for controlling the synthesis of aragonite:vaterite and aragonite:calcite ratios.

The evolution of the precipitates over time lead us to conclude that this system is described by classical growth with twinned aragonite and spherulitic vaterite and aragonite. Solutions with a low water activity can be used as a switch for control of polymorph and morphology and thus define new possible pathways for biomineralization processes.

![Figure 1: Vaterite precipitated in (a) 10% and (b) 50% alcohol under vigorous shaking. With gentle shaking, vaterite did not form in experiments with 50% alcohol.](image)

**Electron donating properties of humic substances and implications for pollutant phototransformation**

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Humic substances (HS) play a key role in many biogeochemical and pollutant electron transfer reactions. Past research primarily focused on HS redox properties under anoxic conditions. This contribution will present the results of a systematic characterization of the electron donating properties of a diverse set of HS under oxic conditions and, for selected HS, relate their antioxidant properties to inhibitory effects on the indirect phototransformation of organic pollutants.

Electron donating capacities (EDCs) were measured by electrochemical oxidation using 2, 2'-azino-bis-(3-ethylbenzthiazoline-6-sulphonic acid) radicals to mediate electron transfer from HS to the working electrode [1]. The number of oxidizable moieties at constant pH and applied reduction potential, \(E_h\), increased from microbial to terrestrial HS and was highest for mixed aquatic-terrestrial HS. For a given HS, EDC values increased with increasing pH and \(E_h\). Strong positive correlations of EDC with HS titrated phenol contents and, for mixed terrestrial-aquatic HS with aromaticities indicates that phenols and hydroquinones are the major electron donating moieties in HS.

HS may decrease indirect phototransformation rates of organic pollutants by donating electrons to oxidized reaction intermediates [2]. Combined electro- and photo-chemical experiments with anilines as model pollutants showed that the inhibition efficiencies of HS on pollutant phototransformation increased with their EDCs. Furthermore, the inhibition efficiency for a given HS increased with increasing pH, in parallel with increasing EDC. Pre-treatment of HS with chemical oxidants, including ozone and chlorine dioxide, reduced the number of electron donating moieties, reflected by significant reduction in both inhibition efficiency and EDC values. These results suggest that EDC and inhibition efficiency on organic pollutant phototransformation are determined by the number and potential distribution of hydroxybenzene moieties present in HS.

Sulfur isotope data from Beaver Brook Antimony deposit, Central Newfoundland, Canada: A hint for the source of mineralization?

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The Beaver Brook Mine exploits one of the largest antimony deposits in the Americas. It has a current production level of 12,000 metric tons antimony concentrate (grading around 65% Sb) per year with current reserves sufficient for an estimated ten-year operating life. The mineralization (dominantly stibnite with traces of pyrite as well as quartz and carbonate gangue) is hosted by meta-sedimentary rocks of Ordovician to Silurian age and structurally controlled by faults and breccia zones. The conditions of formation of the deposit remain unknown, but it has characteristics similar to other Sb-dominated hydrothermal deposits that form at variable temperatures (100-400°C).

Stable sulfur isotope data of ten monomineralic stibnite samples were analyzed at the Department of Mineralogy, TU Bergakademie Freiberg. δ34SVT values for the stibnite samples occupy a very narrow range from -6.6 to -6.0‰ with an total analytical error of ±0.3‰. The narrow range of δ34S values of stibnites from Beaver Brook suggests stable physico-chemical conditions as well as a large well-mixed sulfur reservoir. Obolensky et al. [1] suggest that mixing of neutral or alkaline metal-containing fluids with H2S-bearing fluids sourced from sulfide-rich host rocks are well-suited for stibnite ore deposition. Accordingly, we suggest that the sulfur contained in the Beaver Brook deposit was provided by meta-sedimentary host rocks. The metal source, on the other hand, remains unconstrained [2, 3].


Sediment-water nutrient and Oxygen fluxes in two Antarctic continental shelf areas differently affected by climate change

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Larsen A and B ice shelves, in the Eastern Antarctic Peninsula (EAP), collapsed in 1995 and 2002, respectively. In 2006, during Antarctic expedition ANTXXIII/8, respiration experiments were carried out onboard R/V Polarstern to measure nutrient and oxygen water-sediment fluxes beneath the extinct Larsen ice shelves and off of the Northern Antarctic Peninsula (NAP), a region which has been free of ice shelves in the last 1000 years [1, 2]. Nutrient and oxygen water-sediment fluxes in EAP were studied to investigate how Larsen ecosystems evolved from a situation of negligible primary production and negligible vertical flux of organic matter to the sea floor under ice shelves [3] to a situation of ongoing primary production after Larsen ice shelves collapse [4]. We found higher nutrient and oxygen fluxes in NAP than in EAP probably related to the higher concentration of particulate organic matter found in NAP sediments [5]. Studies on benthic recolonization after iceberg scouring events suggested that the recovery time for an Antarctic mature benthic community is comprised between 230 and 500 yr [6, 7], with early recovery stages that may take up to 10 yr long, presumably like those found in the EAP benthic ecosystem [8].

Equation of state of water and melting curve of Ice VII based on simultaneous measurements of sound velocity and X-ray diffraction of Ice VII to 19 GPa and 873 K

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We have measured the sound velocity of H2O by Brillouin spectroscopy using membrane-style diamond anvil cell with resistance heating at elevated temperatures and pressures up to 873 K and 19 GPa. The unit cells of Ice VII and Au were determined by synchrotron X-ray diffraction, using Au as an in situ pressure gauge. All our samples were contained within and chemically insulated from the Re-gasket hole by a gold liner. Measurements of the sound velocity in liquid water have been extended to 8.0 GPa and 873K. We observed, generally, lower velocities (up to 10% at 723 K) than those given by previous studies [1, 2]. The melting of Ice VII was determined by monitoring the sound velocity drop and the disappearance of diffraction pattern of Ice VII upon melting. Our determination of the melting temperatures differ significantly from those given by previous studies [3, 4], with an observed discrepancy of 130 K at 8 GPa. Given the care taken in the present experiments to avoid potential contamination of the water sample due to reactions at high temperatures between the sample and the gaskets and/or pressure gauges, our new measurements likely provide the first measurements on pure water which displays an extended stability field of the solid phase. Thus, our new measurements suggest that the melting curve of H2O at high pressure needs to be reevaluated.


Discussion of Results

The solid - liquid equilibria in the quaternary system K2B4O7-K2SO4-KCl-H2O at 323 K were studied experimentally using the method of isothermal solution saturation. Solubilities and densities of the solution of the quaternary system were measured experimentally. In the phase diagram of the quaternary system K2B4O7-K2SO4-KCl-H2O at 323 K, there are one invariant point E and three univariant curves E1E, E2E and E3E, and three crystallization fields corresponding to KCl, K2B4O7·4H2O and K2SO4 in the studied quaternary system. The experimental results show that K2SO4 has the biggest crystallization field (E2EE1 field) in the phase diagram (Figure 1).

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Figure 1: Phase diagram of the quaternary system K2B4O7-K2SO4-KCl-H2O at 323 K (KB: K2B4O7·4H2O)
Compressibility change in Fe-rich melt and implications for core formation models
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Density measurements
The physical and chemical properties of molten iron play a key role in core formation, the largest chemical differentiation event in the early evolution of the Earth [1]. We have performed density measurements of molten iron containing an appropriate amount of light elements (5.7 wt.% carbon) up to 8 GPa using the in situ X-ray absorption technique [2, 3].

Discussion of the results
A liquid–liquid transition is identified by a significant compressibility increase in the vicinity of the δ-γ-liquid triple point at 5.2 GPa [4]. The observed increased compressibility of the melt is consistent with the reported molar volume difference between δ and γ phases that increases by a factor of 2 along the Fe melting curve between 0 and 5 GPa [5]. This transition pressure coincides with a marked change in the pressure evolution of the distributions of nickel, cobalt and tungsten between liquid metal and silicate melt that form a cornerstone of geochemical models of core formation. The identification of a clear link between molten metal polymorphism and metal-silicate element partitioning implies that reliable geochemical core formation models will need to incorporate the effects of these additional liquid metal transitions.


Diurnal cycle of Strontium/Calcium ratio in a giant clam shell: A superfine pyrheliometer
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Insolation is an important meteorological parameter and a primary determinant of the Earth's climate system. The historical record of insolation in tropical and sub-tropical regions is short. Moreover, it remains difficult to extract solar radiation from past marine environmental proxy, even though past seawater temperature [1], salinity [2], pH [3], and nutrients [4] were successfully estimated from geochemical data of biogenic marine carbonates such as coral skeletons, foraminifera tests, and mollusk shells. Herein, we describe the precise analysis of Sr/Ca ratio by using a NanoSIMS [5] with 2 micro-meter resolution in a cultivated giant clam shell exhibiting striking diurnal variations, elevated as high as 25% relative to the mean, associated with regional hourly solar radiation. This is the finest proxy among all data ever published. Annual variation of the Sr/Ca ratio is also observed in the sample by a 10 micro-meter spot with 50 micro-meter interval, again correlated with daily insolation record with similar amplitude. Light enhanced calcification and elemental transportation processes in giant clam and symbiotic algae may explain these diurnal and annual variations. Therefore, the Sr/Ca ratio of a giant clam shell might be a useful paleo-chemical-pyrheliometer.

An attempt to trace the redox state of the post Marinoan glaciation (≈635Ma) ocean at the Araras platform (Brazil)

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Oceans and atmosphere oxidation in the Ediacaran paved the way for one of the biggest evolutionary leaps in Earth's history – the dawn of animals. In an attempt to trace such a major oxidation event, we investigated carbonate layers deposited at the base of the Ediacaran period which cap Marinoan glacial deposits in central Brazil. The stratigraphic section in the Araras Group comprises 13 meters of pink dolostone overlain by 25 meters of gray limestone, separated by a transition zone of gray dolostone with higher organic carbon content. Well-preserved sedimentary structures along the section indicate a transgressive tract from shallow marine to deep water deposition environments. Applied redox proxies show two different oxidation states along the sedimentary column: oxic in the dolomitic part and dysoxic-anoxic in the limestone, suggesting that respective carbonates have formed in a redox stratified water column. In the transition zone between oxic and dysoxic-anoxic environments, nitrogen, vanadium, manganese, iron and sulfur show successive variations in their concentrations or isotopic compositions. These variations likely record the succession of nitrogenous, manganeseous, ferruginous and sulfidic zones, thus indicating a progressive upward transition from oxic to anoxic conditions. However, some geochemical proxies (e.g. Ce anomaly, Ni/Co) as well as the classical iron speciation redox indicator FeHR/FeT show contradictory results, providing thus conflicting interpretations for our dataset. We explain the different interpretations of the data in terms of either a paleo-redox state for the post Marinoan Ocean, or a diagenetic overprint.

Metamorphic evolution recorded by amphiboles in the metadolerites from the Frido Unit ophiolites (Southern Apennine-Italy)

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Metadolerites of the Frido Unit Ophiolites have different kinds of texture reflecting various degree of crystallinity. Primary clinopyroxene is replaced by brown and green amphiboles interpreted as being of oceanic origin; brown amphiboles show Mg-hastingsite, edenite, pargasite, Fe-hastingsite, Mg-horneblende and tschermakite compositions, whereas green amphiboles show Mg-hastingsite, hastingsite, edenite, Mg-horneblende, tschermakite and Fe-tschermakite compositions. The blue amphibole rims of the brown amphibole has a winchite and barrowisite compositions; we infer that it crystallized during the early stages of the orogenic metamorphism, likely under static conditions. The different composition of amphiboles occurring in the metadolerites suggest that the ophiolitic rocks from the Frido Unit has been affected by both ocean-floor metamorphism in the amphibolite to greenschist facies conditions and subsequent orogenic metamorphism under HP/LT conditions.
**Multidisciplinary study of Santa Eulalia Plutonic Complex (Central Portugal): Preliminary insight**

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The Santa Eulália Plutonic Complex (SEPC) is a late-Variscan calcalkaline granitic body that occupies an area of 400 km\(^2\) and is located in the Variscan Iberian sector. The host rocks of the complex are composed by metamorphic formations from Proterozoic to Lower Paleozoic. The SEPC has two main facies which present different compositions and textures. From the rim to the core, there is a medium- to coarse-grained pinkish granite (G0) involving large masses of mafic to intermediate rocks and a central gray monzonitic granite (G1). The central facies can be divided into a porphyritic facies (G1A) and a central medium-grained facies (G1B). Multidisciplinary studies that include petrography, mineral and whole-rock chemistry, Anisotropy of Magnetic Susceptibility (AMS) and microstructural analyses were carried out. Besides petrographic and mineral chemistry data, whole-rock analytical results reveal clear differences between these two main granitic facies. G0 granites represent more evolved liquids (>SiO\(_2\) wt.% and <MgO wt.%), plot closer to metaluminous and A-type fields, and present negative Eu anomalies, while G1 facies are typically monzonitic granites with a strong peraluminous character. The AMS study was based on 50 sampling sites. The magnetic susceptibility ranges between 55.09 and 7343.67 \(\times 10^{-6}\) SI. Two major groups can be established: facies G0, with \(K_m > 10^{-3}\) SI which supports the presence of magnetite, and the central facies (G1A, G1B) with \(K_m < 10^{-4}\) SI. In the central facies the paramagnetic behaviour is due to ferromagnesian minerals, such as biotite, and ilmenite. Magnetic anisotropy ranges between 2.2 and 18.2% being in mean >5% in facies G0 and <4% in the central facies. The high P% in G0 facies may be caused by the magnetic bearer, magnetite. Nevertheless, microscope observations show signs of a post-magmatic deformation in G0. These preliminary data support that the facies G0 and the central facies (G1) have a distinct magnetic behaviour which may suggest different redox conditions in magma genesis.

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**Fe(II) and organic exudates interaction in seawater**

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Fe(II) oxidation kinetic was studied in seawater and in seawater enriched with exudates excreted by *Phaeodactylum tricornutum*. The exudates produced after 2, 4 and 8 days of culture at 6.21 \(\times 10^7\) cell/L, 2.29 \(\times 10^8\) cell/L and 4.98 \(\times 10^8\) cell/L were selected. The effects of the pH (7.2-8.2), temperature (5-35°C) and salinity (10-36.72) on the Fe(II) oxidation rate were studied. All the data was compared with the results for seawater without exudates (seawater control). The Fe(II) rate constants decreased as a function of culture time and cell concentration at different pH, temperature and salinity. The experimental data was fitted to a polynomial function in order to quantify the fractional contribution of the organic exudates from the diatoms to the Fe(II) oxidation rate in natural seawater. Experimental results showed that the organic exudates excreted by *Phaeodactylum tricornutum* affect the Fe(II) oxidation, increasing the life time of the Fe(II) in seawater. A kinetic model approach was carried out in order to account for the speciation of each Fe(II) species together with its contribution to the overall oxidation rate.
Biomineralization of Mn oxides by Mn(II)-oxidizing fungi
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Manganese (Mn) oxides are environmentally abundant, highly reactive mineral phases that play important roles in the biogeochemical cycling of nutrients, contaminants, carbon, and numerous other elements. The oxidation of Mn(II) to these sparingly soluble, nanocrystalline MnIII/IV oxide phases is believed to be largely driven by microbiological activity. The majority of studies thus far have focused on the contributions of bacteria to the biogeochemical cycling of Mn, however recent studies have suggested that fungi may substantially contribute to the biomineralization of Mn oxide minerals in some environments. Understanding the environmental impact of these fungally precipitated mineral phases requires detailed analysis of their size, composition, and structure.

Several species of Mn(II)-oxidizing Ascomycete fungi were isolated from metal-contaminated and freshwater environments. A microscopic examination of these fungi revealed that the patterns of Mn oxide deposition varied amongst the different species. In this study, representative Mn(II)-oxidizing fungi were grown under the same chemical and physical conditions to determine if the species of fungus impacts the size, morphology, or structure of Mn biooxides. A combination of electron microscopy and synchrotron radiation X-ray absorption spectroscopy (SR-XAS) were utilized to characterize the Mn oxide phases produced by these representative fungal species.

Our study reveals that the initial phase produced by different species of Mn(II)-oxidizing fungi grown under the same conditions is a highly disordered, nanocrystalline phyllosilicate oxide similar to δ-MnO2. Amongst the different species, however, differences in mineral size, morphology, and secondary products are observed. Changes in solution chemistry (e.g., Mn concentration) further impacts the structure of these biominerals, which could translate to large influences on biogeochemical processes in the environment.
Deep ground water migration in Brazilian Federal District based on isotope geochemistry

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The young capital of Brazil is placed geographically in the Brazilian Central Plains, where the average altitude is close to a 1,000 m above sea level. The area includes drainages that flow to three of the most important river basins of the country: the Paraná, the Amazon, and the São Francisco river basins. Because population has already reached more than 2 million people and continues to grow, policy makers increasingly use groundwater reservoirs.

In order to evaluate the geochemical stability of these reservoirs, we performed an 18 month detailed monitoring of δ¹³C, δ¹⁸O, δD and ⁸⁷Sr/⁸⁶Sr isotopic composition. The isotopic data revealed two main behaviors of these reservoirs: 1) those that present a narrow range of isotopic variation; and 2) those that present a wide range of isotopic variation. While the former were interpreted as isotopic equilibrated water-host rock reservoirs, the later were interpreted as reservoirs that did not reach isotopic equilibrium due to the young age of their waters. We further show that isotopic fluctuation observed in these reservoirs may be related to changes in hydrostatic pressure induced by seasonal variations of rainfall amount.

Biogeochemical and microbial controls of ¹²⁹I mobility in groundwater

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Due to its long half-life (17 My), high mobility, and biophilic properties, ¹²⁹I, a major by-product of nuclear fission, is one of the three major risk drivers at nuclear disposal sites. In aquatic environments, iodine (I), mainly exists as I⁻, IO³⁻ and organic iodine (OI). Field and laboratory batch and column studies were established to understand the inter-conversion of I species in an ¹²⁹I-contaminated plume located in F-area of the Savannah River Site (SRS), by determining speciated ¹²⁹I and stable ¹²⁷I using GC-MS [1]. These studies demonstrated that the mobility of I species greatly depended on the I concentration used [2, 3]. It was found that bacteria isolates can accumulate I⁻ at environmentally relevant concentrations (0.1 µM I⁻); some isolates were also found to oxidize I⁻ to IO³⁻ [4]. When the hypothesis that I mobility can be controlled through an engineered barrier system was tested, results showed that while the majority of I (as ¹²⁷I and ¹²⁹I) existed as I⁻ near the source term, iodide transformed into iodate and organo-I downgradient [5], and was removed through the formation of immobile particulate OI and partly released as mobile OI [6], depending on aromaticity and relative hydrophobicity; the greater the aromaticity, the greater the uptake of iodine [7].

Low oxygen fugacity mantle derived auriferous fluids for Archaean Orogenic Gold deposit of Ajjanahalli, Chitradurga Schist belt, Dharwar Craton, India

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The BIF hosted Ajjanhalli gold deposit of Chitradurga Schist Belt, Dharwar Craton, India has been grouped under Orogenic type of gold deposit in an Archaean set up [1]. Recently magma/mantle origin has been proposed [2] for the source of CO2 rich auriferous fluids based on (13C values of carbonates (-5.1±1.4‰) and the fluid (-5.81±1.14‰). We present here the REE compositions of same carbonates from the auriferous quartz-carbonate veins (QCVs) and compare them with our previous obtained isotope data to understand the source of the mineralising fluid.

Both the chondrite and PAAS normalized REE plots of the carbonates of QCVS shows distinct positive Eu anomaly. As positive Eu anomaly is seen under low oxygen fugacity condition of fluids [3], we propose that the auriferous fluids responsible for gold mineralisation at Ajjanhalli could be from a oxygen depleted source. The δ13C values of carbonates of these carbonates have also indicated a mantle or a felsic magmatic source of auriferous fluids [2]. Though felsic magma source has also been believed for the ultimate source of auriferous fluids [4], positive Eu anomaly of QCVs goes against such a possibility as granitic magma generated hydrothermal fluids could have shown a negative Eu anomaly. We therefore suggest that auriferous fluids could be from a mantle reservoir under a low oxygen fugacity condition.

Since the Orogenic gold deposit at Ajjanahalli deposit is spatially located on a crustal scale shear zone [1] possibility of a mantle derived auriferous fluids cannot be ruled out.


Oxygen isotopes in perovskites from kimberlites

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Isotopic data (Sr, Nd and Hf) obtained from groundmass perovskites (CaTiO3) within kimberlites have been shown to more accurately reflect the unaltered signature, which has besiegled whole rock studies. However, recent studies have questioned their suitability to represent primary kimberlite magma. In situ trace elements along with Sr and stable O isotope data have been employed to assess the effects of contamination on perovskites from Orapa and Wesselton kimberlite. Crustal contamination had a minimal role as the samples have an extended range in La/Yb and Sr/Yb rather than scatter around low values. Moreover, lack of any perovskites with elevated δ18O also suggests minimal interaction with upper crustal material.

The δ18O values from Orapa perovskites show two distinct peaks (around +3.6‰ and -0.6‰). Wesselton perovskites in contrast are clustered around δ18O values of +4‰. Perovskite in equilibrium with the mantle has lower δ18O than other common upper mantle minerals. One group of Orapa perovskites and the Wesselton perovskites are interpreted to reflect the δ18O of uncontaminated upper mantle derived kimberlite magma (4.2‰). The negative δ18O values from the second group of Orapa perovskites are attributed to crystallisation of perovskite after magma degassing, rather than to crustal assimilation, magma mixing, cooling or hydrothermal alteration. The Wesselton sills, however, did not suffer significant degassing, at least to the extent to deplete the magma in 18O.
Synthesis of lithium ion-sieves using biogenic birnessite as a precusor

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Lithium (Li) is regarded as one of the most important elements in advanced industries, and its concentration in geothermal water is around 10 mg/L at the maximum corresponding to about 50 times larger than in seawater [1]. In the present work, synthesis of lithium ion-sieve was investigated using biogenic Mn oxides. Biogenic Mn oxides were produced by a Mn-oxidizing fungus, *Paraconiothyrium sp.* WL-2 strain at pH 6.5 [2].

After biogenic birnessite was suspended in LiCl solution, the solid phase was obtained by evaporation at 80 °C for 24 hours and then calcined at 450 °C for 4 or 8 hours. The calcined product was washed with 0.1 mol/L HCl to exchange with Li⁺ to obtain a sorbent as a template for Li⁺ ions. To compare with biogenic birnessite, several types of synthesized Mn oxides, that is, acidic birnessite, ramsdellite, Mn₃O₄, cryptomelane, were investigated as the starting materials in the same manner.

Based on XRD results, LiMn₂O₄ was detected in three products of five before acid washing, that is, derived from biogenic birnessite, acidic birnessite and ramsdellite. The minimum calcination time was required to obtain a pure LiMn₂O₄ phase using biogenic birnessite as a starting material. XRD peaks assigned to LiMn₂O₄ were maintained even after Li⁺ ions were extracted by acid washing.

While products from acidic birnessite sorbed little Li⁺, the products from biogenic birnessite and ramsdellite sorbed Li⁺ more effectively. Some release of Mn²⁺ was observed during sorption of Li⁺ ions on the product derived from ramsdellite. Products derived from biogenic birnessite showed the most effective performance to sorb Li⁺ ions.

Very alkaline condition is required to synthesize ramsdellite, while biogenic birnessite can be produced around neutral pH values. Therefore, biogenic birnessite is a promising geomimetics as starting materials for synthesis of the effective lithium ion-sieves.


Sorption of Sr²⁺ on hydroxyapatite from calcined fish bones at different temperatures

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Hydroxyapatite was produced by calcination of fish bones at different temperatures (400-1100 °C). Higher calcination temperatures reduced the organic matter content but also provided better crystallized hydroxyapatite and larger crystal sizes with less lattice strain. Higher calcination temperatures also decreased the specific surface area and increased the ion-exchange capacity hydroxyapatite. Sorption of Sr²⁺ as a surrogate for radionuclides was investigated with hydroxyapatite calcined at different temperatures. These results demonstrated that lattice strain affects ion-exchange properties at nano-domain level relatively more as compared to its effects on the surface area.

Figure 1: Sorption capacity of Sr²⁺ on hydroxyapatite with different lattice strain.
Study of deep subsurface microbial community under changing redox conditions using quantitative method

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Microbial activity is one of controlling factor for geochemical condition and the change during excavation and backfilling of underground facility. This study aims to evaluate the role of microbes on geochemical evolution around underground facility. We investigate microbial community and redox condition in the borehole drilled from 140m depth gallery of underground research laboratory (URL) in Horonobe area of Hokkaido, Japan.

Redox potential (ORP(obs)) of groundwater changed from oxidized condition (+180mV) to reducing condition (-480mV) in 10 days. Total microbial count also decreases from 6.6x10^5 cells/ml to 3.2x10^4 cells/ml. Quantification analysis using both 16S rRNA and functional genes with real-time PCR shows that the biomass decreased constantly; domain bacteria (16S rRNA), Nitrate reducers (nirS), denitrifiers (nosZ), Metal reducers (Geobacteraceae 16S rRNA) and Methane oxidizers (pmoA). On the other hand, the biomass increased in 5 days and then decreased or be maintained approximately-constant.; domain archaea (16S rRNA), nitrate reducers (nirK), sulfate reducers (dsr), methanogens (mcrA). The change corresponded with redox potential change. These groups would have ecological relationship. Microbial community quickly changes according with redox condition change in deep subsurface.

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Air quality over India: Weekly periodicities and long term trends

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Air quality degradation is emerging to be an issue of major concern in India. This is mainly attributed to unplanned urbanization and industrial growth. Central Pollution Control Board is executing a nation-wide programme of ambient air quality monitoring. This network consists of 342 monitoring stations covering 127 cities in India. In addition, Indian space Research Organisation (ISRO) is maintaining 33 climate observatories across the country namely ARFINET (Aerosol Radiative Forcing over India Network). In this study, we have used multi-year observations of particulate mass (PM) concentration, aerosol black carbon (BC) mass concentration and aerosol optical depth (AOD) from these network observatories to make assessment of ambient air quality over India and its radiative impact. It has been observed that both column AOD and ground-level measurements (BC and PM) exhibit a weekly cycle with low aerosol concentrations on weekends. In comparison to the weekdays, the weekend reductions of AOD, BC and PM were ~15%, 25% and 24%, respectively. Aerosol trends indicates conflicting trends at different regions of India, thereby reflecting the complex factors behind the impact of growth on environment. While an increasing trend in aerosol has been observed in many cities, some cities show a decreasing trend during the last few years. Aerosol radiative impact assessment was made using ground-based radiometers and is compared with that simulated by radiative transfer models (which employ measured aerosol microphysics). One striking inference from this effort is the large discrepancy between observed and modelled aerosol surface radiative impact. Potential sources of such discrepancies are discussed in this presentation. The CHIMERE chemistry-transport model was used to simulate PM, BC and AOD over India and are compared with measurements. Evaluation of CHIMERE output shows that while diurnal and seasonal trends are captured reasonably by the model, absolute magnitudes differ substantially.
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U-Th-Pb analyses by eximer laser ablation/ICP-MS on MG Brazilian xenotime

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Measurements

Several fragments of MG xenotime were mounted in epoxy disk (2.54 cm). Temora, FC and GJ standards were used as reference. The analytical conditions were: RF = 1200 Watts, Cooling gas = 15 L/min, Aux gas = 0.70 L/min, Sample gas flow = 0.75 L/min. Detector configuration: 202Hg = IC3, 204Hg + 204Pb = IC 4, 206Pb = L 4, 207Pb = IC 6, 208Pb = L 3, 232Th = H 2 and 238U = H 4, where IC = MIC, L (low) and H (high) are Multi Faraday Cups. The intensity to 80Ar for stable condition was around 10V (aux gas =0.77 L/min and He gas = 0.65 L/min). The Laser analytical conditions to get the best ablation rate were: wavelength = 193 nm, Energy = 6mJ, Repetition rate = 10Hz, He gas flow = 0.65 L/min, spot size = 38 mm.

Results

The MG crystal shows Th concentration ranging from 300 to 2000 ppm with low common Pb (204Pb/206Pb ratio <0.0001). The Th/U ratio ranges from 0.9 to 4.5. The GJ show low 232Th intensity (~2 mV) but high 238U (150 mV) intensity while MG shows high 232Th (150mV) and normal 238U intensity (90mV). Also the 232Th/238U ratios on GJ zircon standard range from 0.012 to 0.022, while in the MG ratio are much higher ranging from 0.7 to 4.7. The 232Th intensity on GJ zircon standard range from 0.7 to 3 mV, while MG presents 130 mV (gray portions) to 900 mV (brown portions). Electron microprobe analyses, indicate high contents of Dy 2O3 (3 – 6%), Er 2O3 (3-4%), Yb 2O3 (2-3%) and Lu2O3 (0.3 – 0.8%) for MG. The 206Pb/238U weighted average age of 445.8 ± 4.5 Ma using GJ1 as standard, is lower than the TIMS age of 492Ma (1). This difference must be investigate but here it is suggested to be related to matrix effect.

Conclusions

The MG xenotime present a high U content, permitting precision measurements which is very helpful for the beam focusing during the LA-ICP-MS pre-adjustment set up. Therefore its high REE and Th concentrations, require matrix corrections of several percent for data from most zircon samples.


Effects of non-supercritical CO2 on leaching of potential microbial substrates from macromolecular organic matter

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The storage of CO2 in underground reservoirs is discussed controversly in the scientific literature and the public. The worldwide search for suitable storage formations also considers coal bearing strata. In addition, injection of CO2 into coal formations is already applied for enhanced gas recovery of coal bed methane. Nevertheless, processes resulting from increased CO2 concentration especially in organic matter rich formations are rarely investigated.

Depending on reservoir pressure and temperature, the injected CO2 will dissolve in the porewater causing a decrease in pH [1] and resulting in acidic formation waters. Recent investigations outlined the importance of potential substrates (e.g. low molecular weight organic acids) stored in organic-rich lithologies such as coals [2]. Huge amounts of these substrates are chemically bound to the macromolecular matrix and may be liberated by hydrolysis within the acidic porewater. Therefore, injection of CO2 into coal formations may result in an enhanced nutrient supply for microbial metabolism.

To study the effects of high dissolved CO2 concentrations on macromolecular organic matter, we developed an inexpensive, high-pressure high-temperature incubation system. It allows not just controlling hydrostatic pressure and temperature but also the concentration of dissolved gases. Furthermore the system can be used for both static and flow through experiments and also allows subsampling during the experiment without depressurization.

We will present results from leaching experiments of low molecular weight organic acids such as formate and acetate with CO2 saturated water at varying temperature and pressure conditions on coal samples of different thermal maturity.

Aerosol particle phase state measurement technique using a low pressure impactor

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The phase state of aerosols has impact on the behaviour of atmospheric aerosols. Recently published results show that the atmospheric biogenic SOA particles can adopt amorphous solid phase [1]. Existing methods to resolve solvent absorption induced phase change, such as tandem differential mobility analysis rely on the size change of particles related to solvent uptake.

To study the particle phase and phase change induced by size-preserving processes e.g. oxidation, a new method has been developed. The method relies on impaction of particles on a smooth substrate and subsequent counting of bounced particles by condensation particle counter [2].

An example data of bounce probability with varying relative humidity is given in Figure 1. An ammonium sulphate aerosol was cycled through the system and an almost step-like transition was seen on the bounce probability at around 80% relative humidity. This corresponds well with the known deliquescence relative humidity of 80% [3].

The bounce probability can not at present be quantitatively linked to mechanical properties of particles, but it is qualitatively informative. The method has been applied on nebulised laboratory aerosols as well as on SOA.

Figure 1: Fraction of 91nm ammonium sulfate particles detected after impaction with varying humidity

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Gold mobility in the mantle: Constraints from sulfides in pyroxenites and lherzolites

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Sulfides are the host for gold in the mantle [1], yet there is a scarcity of reliable Au analyses for sulfides from different mantle rock types. As a result, the geochemical behaviour of Au in the mantle is still poorly understood. In this study Au has been measured along with major and trace elements in sulfides in the well-characterised peridotite and pyroxenite xenoliths from Qilin, southeastern China. The peridotites are spinel and amphibole-spinel lherzolites, and the pyroxenites are basaltic melts that have re-equilibrated to spinel and garnet websterites in the upper mantle [2].

Pyrrohotite with very limited variability in major-element geochemistry is the dominant sulfide in the pyroxenites. The sulfides in the lherzolites include polyphase assemblages of mainly monosulfide solid solutions (MSS) with minor millerite, hazlewoodite and cubanite. The lherzolite-hosted sulfides have substantial variation in Fe, Ni and Cu contents. Interstitial and enclosed sulfides in these samples are mineralogically and chemically identical.

There are significant differences in the Au content of the pyroxenite- and lherzolite-hosted sulfides. Most pyroxenite sulfides have Au concentrations below lower limits of detection (<200 ppb), whereas the Au concentrations in lherzolite-hosted sulfides are several times higher than detection limits. There is no systematic difference between the Au content of sulfides in samples that have been modally metasomatised (amphibole-bearing), and sulfides in amphibole-free samples.

The lherzolites are quite fertile (equivalent to ~10% melt removal [3]), but there is no consistent trend in the PGEs (average Pd/Pt/Os = 1.49). However Au in these samples does appear to be depleted compared with the PGEs (average Au/Ag = 0.25). This trend in the lherzolites strongly contrasts with the Au/Os ratio in the pyroxenites, where Au is relatively enriched. This comparison between Au in pyroxenite- and lherzolite-hosted sulfides suggests that Au can be transported by melts, and these melts may play a significant role in Au enrichment in the mantle.


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Silicon isotopes in granitoid rocks

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Gravites (and other felsic lithologies) constitute ~50% of the mass of the upper continental crust [1] and play a major role in global weathering [2], yet little information exists on their Si isotopic composition and systematics. In principle, S-type granites (that is, those with a pelitic sedimentary affinity [3]) should be isotopically light, as weathering enriches sediment in the lighter Si isotopes, whereas ‘igneous’ granites (I- and A-type) should be isotopically heavier. Previous work [4] reveals relatively large Si isotopic variation in granitoid rocks, but no systematic differences between granite types - however, the large uncertainties associated with these data makes interpretation difficult.

Here we revisit this problem and provide a Si isotopic perspective on granite petrogenesis with the benefit of high-precision techniques. We have analysed a representative suite of over 30 I- and A-type granitoid samples and mineral separates, using a HF-free alkali fusion method and high-resolution MC-ICP-MS [5].

The data fall between δ30Si = -0.41 and -0.11 ± 0.06‰ (2 s. d. external precision), although the variation within each batholith is small, providing evidence of a strong source control. However, Si isotopes do not distinguish between I- and A-type granites; both groups display a similar range of isotopic compositions. In contrast, the data for A-type granites are more restricted and comparable to extrusive felsic material [6]. A strong negative correlation with initial 87Sr/86Sr provides evidence that Si isotopic variation in both I- and A-type granites can be explained by contamination of an ‘igneous’ source region magma by an enriched (high Rb/Sr) end-member, possessing a light δ30Si signature, such as sediment derived from continental crust.


Volcanic ashes as the source of dissolved calcium in seawater

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The geochemical balance of carbon in the modern ocean indicates that 487 million ton of Corg annually oxidizes and form Ca-Mg carbonates. The reaction of carbonate formation requires 1.628 million ton of Ca (Mg) from silicates. Volcanic terrigenous ashes coming into the ocean possess of great specific surface and can pretend to the role of significant source of labile Ca (Mg). It was tested experimentally.

Variable amounts of ashes were placed into artificial 35‰ seawater containing no borates and salts of weak acids with the exceptions of carbonate. Hermetically closed contents were mixed during a month, and filtered through 0.22 μm filters. Values of pH, Alk, and concentrations of Ca, Mg, and Si were determined both in filtrates and the initial seawater.

Concentrations of calcium and silicon in all experiments increase in direct relation to the solid/water mass ratio (table). Maximal calcium mobilization was observed for the Koryaksky volcano ashes containing 2.1% Sorg. High sulfur content in this sample accounted for dramatic pH and Alk reduction. But pH and Alk reduction was observed also in the experiments with low-sulfur ashes from Kamchatka. This indicates that other reactions may affect acid-base equilibrium. Magnesium concentration except the Karymsky volcano ashes also increases with the solid/water mass ratio increase, but lesser than calcium concentration. Dissolved calcium and magnesium coming into the ocean can possibly bind dissolved inorganic carbon formed by oxidation of Corg of continental runoff in the ocean.

<table>
<thead>
<tr>
<th>Volcano</th>
<th>Mass of ash, g/l</th>
<th>pH</th>
<th>ΔAlk</th>
<th>Δ[Ca]</th>
<th>Δ[Mg]</th>
<th>Δ[Si], μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koryaksky, 2.1% S</td>
<td>10</td>
<td>7.17</td>
<td>-0.80</td>
<td>4.39</td>
<td>0.17</td>
<td>94.4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>6.79</td>
<td>-1.48</td>
<td>8.89</td>
<td>0.51</td>
<td>143.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>5.92</td>
<td>-2.30</td>
<td>21.55</td>
<td>1.82</td>
<td>263.5</td>
</tr>
<tr>
<td>Ksudach, 0.022% S</td>
<td>10</td>
<td>7.56</td>
<td>-0.22</td>
<td>0.34</td>
<td>0.09</td>
<td>86.9</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>7.45</td>
<td>-0.42</td>
<td>0.57</td>
<td>0.14</td>
<td>128.6</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>7.24</td>
<td>-0.84</td>
<td>1.03</td>
<td>0.26</td>
<td>211.2</td>
</tr>
<tr>
<td>Karymsky, 0.085% S</td>
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<td>7.49</td>
<td>-0.02</td>
<td>0.11</td>
<td>&lt;0.02</td>
<td>26.4</td>
</tr>
<tr>
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<td>7.43</td>
<td>-0.16</td>
<td>0.23</td>
<td>&lt;0.02</td>
<td>43.4</td>
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<tr>
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<td>7.32</td>
<td>-0.38</td>
<td>0.34</td>
<td>&lt;0.02</td>
<td>86.4</td>
</tr>
<tr>
<td>Eyjafjallajökull, 0.076% S</td>
<td>10</td>
<td>7.61</td>
<td>0.10</td>
<td>1.14</td>
<td>0.57</td>
<td>89.3</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>7.60</td>
<td>0.14</td>
<td>1.82</td>
<td>0.88</td>
<td>125.4</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>7.61</td>
<td>0.19</td>
<td>3.19</td>
<td>1.08</td>
<td>155.6</td>
</tr>
</tbody>
</table>

Table 1: Variation of seawater composition at the interaction with volcanic ashes.
Tracing deep slab recycling via study of boron isotopes of volcanic rocks from hotspot (OIB) settings

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Boron and B isotopes have potential to be among the best tracers of fluids and crustal components in the deep mantle because isotopically light B, strongly fractionated at the slab or isotopically heavy B, imprinted in the wedge could be recycled. Analytical challenges in basaltic rocks are presented by low B concentrations, and only limited high precision B isotope ratios are reported for OIB volcanic suites [1, 2]. Hence B and B isotopes have not been widely used to quantify potential slab and crustal contributions to hotspot magmas. Here we report LA-ICP-MS and TIMS δ11B ratios and SIMS B concentrations for OIB lavas from key hotspot sites representing end-member components of the various mantle reservoirs. The B contents are always low (generally <5 ppm) and the δ11B ratios are as follows: Society Isl. (+1.3 to -7.7‰; n=10); French Polynesia-Samoa Isl. (+2.8 to -9.1‰; n=10); Mt.Erebus/McMurdo Group/Cravy Mts. (+2.3 to -10.4 ‰; n=10); St.Helena Isl. (+19 to -3.8‰; n=5); Reunion Isl. (-1.4 to -10.2‰; n=2) and Gough Isl. (-3.9 to -8.1‰; n=7). Interestingly, our new B and B isotope dataset often shows large deviations from currently accepted intraplate B and B isotope values for the deep mantle [3]. We shall evaluate the impact of processes such as assimilation of seafloor-altered basement and ancient subduction-related metasomatism as possible causes for the observed isotope variations. The overall negative B isotope results, combined with mantle-like Sr and Nd isotope ratios, indicate very sufficient and large volume B losses during the initial (shallower) stages of subduction, confirming the fluid mobile nature of this important slab tracer.


Seasonal dynamics of sulfide oxidation processes in Tokyo Bay dead zone sediment

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Sulfide (H2S) pool in Tokyo Bay dead zone sediment changed dramatically according to the season (Fig. 1). In early fall with hypoxic bottom water, sediment surface was covered with *Beggiatoa* massively, indicating biological H2S oxidation with NO3-. During winter with oxic bottom water, ascorbate-extractable-iron oxide (Asc-Fe(III)), that reflects ferrhydrite (high reactivity towards H2S, insulative), showed a seasonal maximum, indicating chemical H2S oxidation with Fe(III). During late fall, oxalate-extractable-Fe(III) (Oxa-Fe(III)), that reflects magnetite (low reactivity towards H2S, conductive), showed a remarkable increase with a unique pH signature, pH maximum at oxic-anoxic interface (Fig. 2). Those results suggest that the main process for H2S oxidation during transition period from hypoxic to oxic bottom water was probably bioelectrochemical reactions with O2. H2S oxidation processes in Tokyo Bay dead zone sediment are dynamically shifting in response to O2 conditions in the bottom water.
The role of impurity atoms in forming cation vacancies in the pyrrhotite

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Synthetic pyrrhotites (Fe,S) not containing interstitial atoms in the crystal structure and natural pyrrhotites of the ‘Blagodatny’ mine containing interstitial point defects have been investigated in the stable phase. The phase and chemical composition was monitored by using the methods of X-ray diffraction (XRD) and X-ray spectrum analysis (XRS).

As a result of comparison of the crystal structure and the phase composition of the synthesised samples with natural pyrrhotites the influence of the inclusion atoms on the concentration of cation vacancies has been established.

The influence of impurity atom on the concentration of the cationic vacancies was considered on the basis of calculating the thermodynamic potentials using the Bose-Einstein quantum statistics. The theoretical calculations were compared with X-ray analysis data (Table 1).

<table>
<thead>
<tr>
<th>S/Fe ratio</th>
<th>defects mass, %</th>
<th>sum of defects</th>
<th>impurity atom</th>
<th>cationic vacancies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.130</td>
<td>0.160</td>
<td>0.1038</td>
<td>0.0020</td>
<td>0.1018</td>
</tr>
<tr>
<td>1.140</td>
<td>0.168</td>
<td>0.1185</td>
<td>0.0021</td>
<td>0.1164</td>
</tr>
<tr>
<td>1.147</td>
<td>0.151</td>
<td>0.1284</td>
<td>0.0021</td>
<td>0.1213</td>
</tr>
<tr>
<td>1.154</td>
<td>0.176</td>
<td>0.1234</td>
<td>0.0022</td>
<td>0.1212</td>
</tr>
<tr>
<td>1.152</td>
<td>0.143</td>
<td>0.1326</td>
<td>0.0022</td>
<td>0.1304</td>
</tr>
<tr>
<td>1.160</td>
<td>0.166</td>
<td>0.1389</td>
<td>0.0023</td>
<td>0.1366</td>
</tr>
<tr>
<td>1.158</td>
<td>0.155</td>
<td>0.1366</td>
<td>0.0024</td>
<td>0.1342</td>
</tr>
<tr>
<td>1.164</td>
<td>0.177</td>
<td>0.1412</td>
<td>0.0025</td>
<td>0.1387</td>
</tr>
<tr>
<td>1.164</td>
<td>0.178</td>
<td>0.1411</td>
<td>0.0026</td>
<td>0.1385</td>
</tr>
<tr>
<td>1.157</td>
<td>0.186</td>
<td>0.1363</td>
<td>0.0028</td>
<td>0.1335</td>
</tr>
<tr>
<td>1.180</td>
<td>0.415</td>
<td>0.1529</td>
<td>0.0062</td>
<td>0.1467</td>
</tr>
</tbody>
</table>

Table 1. Results of theoretical calculations on the basis of X-ray analysis of samples (XRS and XRD).

As it is shown in the table, tendency to increase of concentration cationic vacancies with increase impurity atom is calculated on the basis of experimental results.

The influence of S on silicate melt structure: An experimental and spectroscopic approach

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Sulfur is one important volatile element after C and H in magmatic systems, however its effects on silicate melt structure and magmatic physical properties are poorly addressed. We present preliminary result of the effect of sulfur on silicate melt structure based on an experimental approach and spectroscopic measurements.

Glasses of HPG8 and An-Di eutectic compositions were synthesised at 300 MPa and 1250°C and under oxidising conditions (AFMQ+3.0) using IHPV. Starting compositions were equilibrated with a fluid phase composition: S (0 to 5 wt.%) and H2O (5 wt.%). Recovered glasses were characterised using EMPA to determine S solubility, FTIR for H2O solubility, Raman and Solid State NMR for glass structure.

S solubility determined in glasses changes from 0 to 1100 ppm and 0 to 8700 ppm for HPG and An-Di, respectively. The increase in S solubility is accompanied by the decrease in the H2O content from ~5 to 4 wt.% H2O. S is directly correlated to the initial S content traducing the change in the fluid phase composition.

Analyses of fluid inclusions suggest S is present as SO2 and metallic S in HPG and An-Di glasses and additional H2S has also been identified in some inclusions for An-Di glasses. The S speciation within the glasses is only represented by Mn+SO4 groups (Mn+ is Ca2+ in An-Di, Na+ in HPG) consistent with the oxidising conditions of the experiments.

Raman and NMR analyses of the glass structure show subtle changes upon S dissolution. We observe 1) a slight polymerization with increasing S content, 2) a decrease in 31Al in An-Di and 3) a change in the H environments with increasing S content. The observed changes may be the result of decreasing H2O content. However, the subtle changes remain very small suggesting that S will produce only minor changes to the melt structure in comparison to H2O effect. Hence, the change in magmatic viscosity upon S dissolution is likely to be small.
Subducted serpentinites are the boron reservoirs for arc magmatism

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Serpentinites are key players in volatile and fluid-mobile element cycles in subduction zones. Their dehydration represents the main event for fluid and element flux from slabs to mantle, though no direct proof of this fact yet exists. For this purpose, B isotopes are known markers of fluid-assisted element transfer during subduction. Until recently, the altered oceanic crust has been considered the main $^{11}$B reservoir for arc magmas, which largely display positive $\delta^{11}$B. However, slab dehydration below fore-archs transfers $^{11}$B to the overlying hydrated mantle and leaves the residual mafic crust very depleted in $^{11}$B below sub-archs. The $^{11}$B-rich composition of serpentinites candidate them as the heavy B carriers for subduction. Here we present high positive $\delta^{11}$B of Alpine high-pressure (HP) serpentinites recording subduction metamorphism: we show a connection among serpentinite dehydration, release of $^{11}$B-rich fluids and arc magmatism. In general, the $\delta^{11}$B of these rocks is heavy (16‰ to + 24‰ $\delta^{11}$B). $^{87}$Sr/$^{86}$Sr ranges from 0.7044 to 0.7065, i.e. lower than oceanic serpentinites formed from seawater. Our data suggest two implications. 1st, the analyzed HP serpentinites are $^{11}$B reservoirs for subduction. They maintain high $^{11}$B down to a first fluid release event, thus the $\delta^{11}$B of olivine-veins, that fingerprint the composition of released fluids, justify the positive values observed in many arc lavas. Fluids released by dehydration of such HP serpentinites by full antigorite breakdown should have up to + 20‰ $\delta^{11}$B. The comparable $^{11}$B fingerprint of serpentinites, their fluids and arc lavas provides a strong link between subterrigenous subduction and arc magmatism. 2nd, the combination of $\delta^{11}$B, $\delta^{8}$D, $\delta^{8}$Sr/$^{86}$Sr of the HP serpentinite apparently favour their location above the subducting slab. This implies that serpentinites were formed by low-T fluids likely arising from a subducting lower plate.

A new Br isotope analytical protocol: Constraints on the global Br cycle

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Bromine possesses a chemistry broadly comparable to that of Cl and F, however its heavier mass and lower abundance results in slightly different behaviours in the geochemical cycling. Hence it is disproportionately enriched in sea water with respect to Cl, and unlike F possesses isotopes which may be fractionated by geological processes. These isotopes are $^{79}$Br (50.686%) and $^{81}$Br (49.314%).

Br can be considered to be a ‘hydrophile’ element, and hence its behaviour is in many ways analogous to that of water. Therefore environmental (low temperature) aqueous processes, particularly transpiration, weathering and evaporation are likely to produce fractionations in $\delta^{81}$Br of the order of ~3.5‰ [1]. These signatures may be inherited by hydrous fluids derived from subducted slabs in regions where extensive hydrothermal alteration and/or carbonate deposits are present in the downgoing slab.

This study has developed new chemical extraction, and most significantly, new mass spectrometric protocols for Br isotopes on silicates and waters using N-TIMS methodologies. Existing CF-IRMS methodologies offer internal precision of ~0.3‰ (1SD, [1]), whereas N-TIMS measurements of laboratory HBr and seawater standards produce external reproducibility of <0.07‰ (1SD) over a 6 month period with internal precision typically <0.06‰ (1SD) on single analyses.

Southern Hemisphere Pacific Ocean Water (SHPOW) records $81$Br/$82$Br significantly lower (0.9627) than the IUPAC canonical ratio (0.9729; a difference of ~10‰).

Protocols for mitigation of PO$_3$-polybaric interferences on $81$Br- will also be presented, as will $81$Br data for depleted Island Arcs Tholeiites.

High-precision $^{10}$Be-dating of moraines and the exploration of pro-glacial bedrock as climate archive using the new in situ $^{14}$C/$^{10}$Be tool

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$^2$Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania, USA
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Methodological and analytical progress in cosmogenic nuclide techniques has surged in recent years, fueled in part by the CRONUS initiatives. One example is the increase in sensitivity of the $^{10}$Be and the in situ $^{14}$C methods that affords new perspectives on glacier fluctuations in response to past climate change. Moraine records around the globe can now be dated with unprecedented precision and pro- and subglacial bedrock can be explored as climate archive for past warm periods.

Here we present published and unpublished glacier chronologies from southern and northern mid-latitudes. The chronologies show centennial resolution of past glacier advances. The proglacial bedrock data yield complementary informations about periods of smaller-than-today glaciers.

We discuss the climatic implications of these data sets, focusing on (i) the chemical and analytical protocols behind this advance, (ii) the high internal consistency of the chronologies and the underlying reasons, and (iii) perspectives towards further method progress and its relevance for climate science.

Modeling of alteration processes in the Ringelbach granitic research catchment (Vosges, France)

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A geochemical modeling approach has been used to characterize the nature of weathering processes occurring within the Ringelbach granitic catchment (Vosges, France). The main springs were regularly sampled over the 2004-2006 period and analysed for major and trace element concentrations and Sr and U isotope ratios. Water samples from two 150-m deep boreholes drilled within the watershed were also used and analysed for this study; Geochemical characteristics of the waters are systematically different among the springs (depending on their elevation along a same slope) and deep boreholes (Chabaux et al. this issue).

The coupled transport/reaction model KIRMAT [1, 2] allows us to discuss and constrain the origin of such a systematic geochemical variation. The KIRMAT model combines geochemical reactions and one dimension mass transport equations to simulate the reactive transport of a fluid through a rock along a given water pathway. It was also designed to incorporate ideal solid solutions for the precipitation of clay minerals [3]. In the case of the Ringelbach weathering, the model simulates the transport of rainwaters along a 1-D water pathway crossing the different weathering levels of the granitic bedrock, from the surface saprolite level to the deep fresh granite. The long-term simulations (30ky) lead to weathering mineralogical sequences and to porosity evolution of the granitic bedrock consistent with field observations. They also point out that the geochemical characteristics of the water samples collected on the Ringelbach catchment depend on both the lithological level in wich the waters circulate and on the duration of the water transfert within each lithological level. The latter is certainly a key parameter to be further addressed in future studies.

Formation of secondary minerals
A lysimeter approach

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Heavy metal contamination of large areas due to uranium mining operations poses a serious long-term environmental problem. In Ronneburg, in eastern Thuringia, Germany, leaching of low grade uranium bearing ores (uranium content < 300g/t) proceeded from 1972 to 1990 using acid mine drainage (AMD; pH 2.7-2.8) and diluted sulphuric acid (10g/l). Secondary mineral phases like birnessite, todorokite and goethite occur as natural attenuation process associated with enrichment of heavy metals, especially Cd, Ni, Co, Cu and Zn due to a residual contamination even after remediation efforts.

To reveal the processes of secondary mineral precipitation in the field a laboratory lysimeter approach was set up under similar conditions than in the field. Homogenated soil from the field site and quartz were used as substrates. Water supply was just from the bottom by a marriot’s bottle using contaminated groundwater from the field. Evaporation processes were accepted to allow continuous flow of water. This leads to precipitation of epsomite and probably aplowite on the top layer equal to field investigations. In situ measurements of redox potentials showed in general high oxidizing conditions (200-750 mV) due to different redox couples in the groundwater. After 4 weeks first secondary minerals became visible. Although Eh/pH data does not support formation of manganese minerals, SEM-EDX data show microorganisms in organic rich phases together with the occurrence of manganese, oxygen and nickel, indicating manganese oxides enriched in nickel. Infrared (IR) spectroscopy give hints for todorokite of being the secondary manganese mineral. Soil water samples were used for monitoring behavior of metals within the lysimeter. Hence saturation indices (SI) for different secondary minerals were calculated with PHREEQC. Clay minerals (e.g. kaolinite, illite) show SI values up to 5 indicating precipitation. This is coincided with a nearly completely depletion of aluminum in the soil water after entering the lysimeter and XRD measurements. The SI of goethite also shows oversaturation with respect to the soil solution. SEM-EDX analyses and IR spectroscopy confirm the formation of goethite. Data revealed that the formation of goethite is mainly dominated by Eh/pH processes in this system and that heavy metals like Zn and U could be enriched.

Are Large Igneous Provinces net-sinks for CO2?

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Continental flood basalts are subaerially erupted Large Igneous Provinces (LIPs), often covering significant continental areas with millions of cubic kilometers of lava. Recent evidence from the Central Atlantic Magmatic Province (CAMP) record in the Eastern North American (ENA) Newark Rift Basin demonstrated that LIPs may result in a transient doubling of atmospheric pCO2, followed by a ~300 ky falloff to near pre-eruptive concentrations (J). We use the pedogenic carbonate paleobarometer in the corollary Hartford Basin to confirm findings in the Newark, and to test the million-year scale effect of the CAMP eruptions.

We find that the Hartford basin pCO2 record is consistent with observations from the Newark, where a ~4400 ppm pCO2 peak is identified just after each volcanic episode. The significantly longer post-extrusive Portland formation of the Hartford Basin shows a fourth CO2 pulse to ~4500 ppm, about 250 ky after the last lava recorded in the ENA section, which may correlate to a later basalt in the Central High Atlas Basin of Morocco. The Hartford record also shows a rapid post-eruptive decrease in pCO2, reaching pre-eruptive background concentrations of ~2000 ppm in <~300 ky, consistent with observations from the Newark Basin. Furthermore, the Hartford post-extrusive section exhibits a long-term decrease in pCO2 to levels below the pre-CAMP background over the subsequent 1.5 My following the final apparent episode of eruptions.

We use a simple geochemical carbon-cycle model to demonstrate that the rapidity of these decreases, and the fall to concentrations below background may be accounted for by a 1.5-times amplification of continental silicate weathering due to the presence of the CAMP basalts themselves. If basalt has 10-times the chemical reactivity of continental crust, such an amplification would require eruption of lavas over an aerial extent of ~8.3 x106 km2, well within independent estimates of the CAMP at 1.1 x 107 km2. Together, these results indicate that continental flood basalts result in an extreme short-term perturbation of the carbon system, followed by a long-term decrease in pCO2 to below pre-eruptive levels, implying they may have an overall net-cooling effect on global climates.

Alkaline mantle melts pinpoint late Triassic thinning of the Southern Alpine lithosphere (Ivrea Zone, Italy)

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4Museo Cantonale di Storia Naturale, Lugano, Switzerland

Following granulite facies metamorphism and abundant mafic magmatism in the Permian lower crust, the European – Adriatic continental crust thermally equilibrated prior to upper Triassic to lower Jurassic rifting and exhumation. During this process, decompressional partial melts from the asthenosphere intruded into the lower continental crust and locally triggered partial melting and rejuvenation of isotopic systems. Such features have been described from the Ivrea zone [1, 2].

We studied Na-rich peralkaline leucocratic pegmatoid lenses within the ultramafic Finero body (N-Italy/S-Switzerland) at the eastern end of the Ivrea zone. These pegmatoids are composed of nepheline, plagioclase, biotite, zircon, apatite, sodalite and corundum. High-precision U-Pb ID-TIMS age determinations on single crystals, fragments and zircon, apatite, sodalite and corundum. High-precision U-Pb ID-TIMS age determinations on single crystals, fragments and zircon crystal - are compatible with a first emplacement of isotopic systems. Such features have been described from the Ivrea zone [1, 2].

Estimating stable isotope signatures of core formation

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The geochemical separation of isotopes at equilibrium is a process driven by material dynamics, chiefly the zero-point energy of vibrations (phonons). Isotopic signatures caused by this process might be useful for understanding the composition and conditions of formation of the Earth’s core, as well as metal-silicate segregation elsewhere in the solar system [1-5]. This presentation will discuss recent progress in using first-principles models to understand isotopic fractionation caused by dissolution into metal alloys at high temperatures and/or pressures, as well as complementary techniques including spectroscopy-based modeling, experiments, and empirical calibration. Estimates of H, C, N, O, Si, S and Cr isotope fractionations in iron-rich metallic melts are calculated with density functional theory, via models of iron-rich crystals with high-pressure and thermal expansion – in the case of silicon-isotope fractionation it appears that pressure effects of bonding environments analogous to liquid alloy, e.g. dhcp-FeH, Fe3C-cohenite and Fe3Cr. Alloying atoms in these crystals are completely coordinated by iron. Equilibrium fractionation is assumed to be driven by the reduction of vibrational frequencies when heavy isotopes are substituted – though mass-independent fractionation may become significant for very heavy elements (e.g. platinum group elements, Pb). Quasiharmonic methods approximate the effects of high pressure and thermal expansion – in the case of silicon-isotope fractionation it appears that pressure effects of bond compression and increased cation coordination in silicate melts roughly cancel each other along the mantle liquidus. Stronger pressure effects are possible for other elements. The calculations suggest that iron alloys will usually be depleted in heavy isotopes, relative to other planetary materials, by as much as ~100‰/amu at 2000 K in the case of D/H fractionation between FeH and water, or as little as ~0.1‰/amu in the case of 53Cr/52Cr. Isotopic signatures appear to be largest for light elements (H >> C, N, O >> Si > S, Cr), and at low temperatures. All of the light-element systems studied could show isotopic separations large enough to measure, suggesting that significant core partitioning could perturb the bulk silicate Earth isotopic composition. Experimental and empirical determinations of Si-isotope and C-isotope fractionations broadly agree with theoretical models.


Modeling isotopic signatures of nebular chlorine condensation

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Recent measurements of 37Cl/35Cl in bulk chondrites and the silicate Earth suggest a relatively homogenous distribution of chlorine isotopes1, but significant variation has been found in other planetary samples. In order to assess the potential for stable chlorine isotope ratio measurements to constrain the origin and transport of chlorine in chondritic parent bodies and other planetary precursors, and more broadly in minerals and ices, we calculated equilibrium 37Cl/35Cl isotope fractionations between gas-phase HCl and the crystalline phases HCl.3H2O, NaCl (halite), KCl (sylvite) and Na4Al3(SiO4)3Cl (sodalite) using a combination of experimental vibrational frequencies and electronic structure (DFT) models. Sodalite is estimated to have ~0.7‰ lower 37Cl/35Cl than HCl at ~950 K, the expected 50% condensation point for silicate-hosted chloride. This fractionation is in the same direction, but somewhat smaller than, the ~1.3‰ 37Cl/35Cl depletion observed in primitive sodalite inclusions in Allende1. Calculated halite-sodalite fractionation at 1098 K is also of the same sense but smaller than an experimental calibration (0.02‰ vs. 0.3‰) [1]. In contrast, HCl.3H2O hydrate is predicted to have 3-6‰ higher 37Cl/35Cl than coexisting HCl gas in equilibrium at temperatures relevant to low-pressure gas/crystal partitioning (roughly 140-160 K). This enrichment in ice is opposite in sense to what would be expected in a general rapid condensation process — more mobile 35Cl-bearing molecules with weaker H-Cl bonds should react faster and thus 35Cl should be enriched in the rapid condensation product. It is also opposite in sense to predicted and observed equilibrium isotope fractionation between HCl vapor and liquid water [2], but may overlap fractionation associated with disequilibrium evaporation. These results suggest that it may be possible to distinguish between icy [3] and silicate sources of chloride to planets and planetary precursors, so long as chlorine condensation is not quantitatively complete. Acid hydrate-derived high 37Cl/35Cl signatures, if found, could additionally indicate a post-condensation origin of chlorine-bearing minerals in chondrite minerals, and would be consistent with correlated high chlorine abundances and hydration in CI chondrites.

Growth conditions of stalagmites derived from noble gas concentrations in fluid inclusions

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Stalagmites are increasingly used as climate archives to reconstruct past climate conditions over long time intervals and in wide ranges of continental regions. We analysed noble gases in 43 Holocene samples from 2 tropical stalagmites (D1, P3) from Socotra Island, Yemen. Kr and Xe concentrations in many of the samples are explained as binary mixtures of noble gases from air-saturated fluid inclusion water and atmospheric noble gases released from air inclusions (‘excess air’). After 2-component deconvolution, equilibrium concentrations of noble gases in the fluid inclusion water are calculated, from which in turn noble gas temperatures (NGTs) are deduced [1]. NGTs are assumed to reflect the ambient cave temperature at the time of the last gas exchange.

Many NGTs in D1 and P3 agree with the modern cave temperature (28°C). However, we observe relatively large NGT variations over short time scales, which cannot reflect actual cave temperature variations. We attribute these variations to changing conditions during air-water partitioning between inclusion water and the local cave atmosphere. An occasional enrichment in CO2 around the stalagmite would lower the partial pressures of Kr and Xe and thus reduce their equilibrium concentrations in the inclusion water leading to spuriously high NGTs.

Our analyses also provide a record of the water content and allow to determine the amount of excess air in the samples. D1 shows a statistically significant regime shift at ~1.5 ka BP (see [2] for age model) both in the water content and in the amount of excess air. The regime shift coincides with the most negative excursion in the δ18O record of the calcite [2]. Thus, growth conditions of stalagmite D1 changed dramatically at this time, possibly in response to a reduced drip rate, which lead to a major change in the amount of air and water inclusions incorporated in the stalagmite.


Chromium isotopes in Saanich Inlet sediments and waters

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Saanich Inlet is a classic locality for study of anoxic sedimentation and sulfidic water column processes. Organic-rich sediments from the inlet are enriched in Cr relative to the detrital background. Water column sulfide develops in the summer months as a result of stratification and high primary productivity and restricted deep water renewal. Thus, Saanich Inlet provides an excellent opportunity to uncover the modern behaviour of Cr isotopes, which show promise as a tool for paleoenvironmental analysis with respect to redox cycling. Cr isotopes are fractionated through reduction of soluble Cr(VI) to relatively insoluble Cr(III), enriching the lighter Cr isotopes. This study will be the first to assess the fractionation between Cr in contemporaneous waters and sediments in an anoxic setting.

Preliminary results for total Cr in the water of Saanich Inlet (100 m depth) show a δ53Cr of +0.30‰ (normalized to SRM 979), with a total Cr concentration of 0.11 µg/L. This is a lower concentration than open ocean seawater (North Atlantic Seawater; 0.26 µg/L), suggesting that there may be removal of Cr from the water column. At the time of collection (August 2010), the water column was sulfidic below ~80 m depth. Open ocean Cr [1] has a δ53Cr of +0.45 to +0.71‰, which suggests that Cr in the sulfidic water column of Saanich Inlet is being reduced and removed to the sediments. The Cr leached from the organic component of Saanich sediments was -0.17‰, while bulk marine sediments average -0.03‰ [2]. This system does not conform to the results of groundwater and laboratory experiments performed by others, which yielded large fractionation factors of ~+3.5‰ and predicted sedimentary δ53Cr values of ~+3‰. One possibility is that reduction goes to completion on only a small fraction of the available Cr, perhaps facilitated by water column particulates or processes operating at the sediment-water interface.

The biogeochemistry of phytosiderophores in the rhizosphere in relation to Fe uptake

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Phytosiderophores (PS) are naturally occurring chelators, which are exuded by graminaceous plant species for the sake of iron acquisition (Strategy II) [1]. PS are highly efficient in mobilizing Fe from soil [2], and upregulation of PS exudation is the key iron deficiency stress response mechanism for graminaceous plants [1].

Despite the extensive research on the mechanism of action of PS, the understanding of the biogeochemistry of PS in the rhizosphere is still limited. The vast majority of studies have been carried out under conditions quite remote from those present in the rhizosphere (e.g. with hydroponic systems).

A lack of adequate analysis and sampling techniques, the complicated acquisition of PS from root exudates and the biodegradation of PS by rhizosphere microorganisms are among the principal problems, prohibiting a more detailed study of PS in relation to soil-grown plants.

Our research project addresses several of these issues, amongst others through synthesis of PS ligands, development of new analytical methods suitable for measuring PS and metal-PS complexes in soil solution, and application of novel rhizosphere sampling techniques with rootboxes and microsuction cups.

The overall aim of the projects is an integral quantification of the source and sink terms determining PS concentrations in the rhizosphere. Both reaction kinetics and thermodynamic equilibrium aspects will be considered. Processes that will be examined include adsorption, desorption, mobilization of iron and other metals from the soil, biodegradation, PS exudation and PS-facilitated iron uptake.


Hydrothermally induced changes of electrical rock conductivity and permeability in porous feldspar-rich materials

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Due to the extraction of heat during geothermal energy production from deep sedimentary reservoirs, dissolution and/or precipitation reactions may be induced which potentially alter the pore space properties of the reservoir rocks. In this study hydrothermal batch and flow-through experiments were conducted with feldspar-rich porous materials at temperatures up to ~160°C, under hydrostatic pressure conditions, and durations up to 4 months to investigate the influence of such reactions on electrical rock conductivity ($\sigma_r$) and permeability ($k$).

Sample materials were feldspar-rich Rotliegend sandstone samples and granular analogue materials composed of quartz, K-feldspar, and plagioclase grains. The temperature range applied in the experiments pertains to a low enthalpy geothermal energy production scenario. The starting fluids ranged from deionised H2O to 2 mol/L NaCl aq solutions. $\sigma_r$ was continuously monitored while $k$ was measured at irregular intervals throughout the flow-through experiments. In the batch experiments electrical fluid conductivity ($\sigma_f$) was measured at irregular intervals.

Chemical fluid analyses were performed on the resulting fluids with respect to the major ions of the system H⁺, Na⁺, Al³⁺, Si⁴⁺, K⁺, Ca²⁺, OH⁻, Cl⁻, and SO₄²⁻. Aliquots of the solid materials were characterised prior and after the experiments with XRD, BET, Hg-porosimetry, SEM, and EMPA. Sub µm sized structures on altered grains were also investigated with TEM. One sandstone sample was analysed with X-ray CT with a resolution of ~2 µm prior and after a flow-through experiment to image the pore space in situ.

Dissolution features were common on the altered solid materials while precipitates were rarely observed. Precipitates were sub µm sized amorphous particles occurring mainly on plagioclase surfaces. The transient increases of concentrations of dissolved ionic species, of $\sigma_f$ and $\sigma_r$ indicate a kinetically controlled dissolution process. Concurrently $k$ decreases in the course of the flow-through experiments. The $k$ decrease is mainly due to thermo-mechanical effects but may also result from the observed dissolution and precipitation reactions which lead to an alteration of the geometrical properties of the pore space.
The speciation of Au, Ag, Hg, Th and U in peat polluted by acid mine drainage

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The peat substance is one of the more popular natural sorbents that is used to recovery of elements from aqueous solutions including other similar materials. Ursk’s sulfide-bearing waste piles (Ursk, Kemerovo region, Russia) have been formed more 50 years ago. The wastes of the cyaniding primary Cu-Zn-polymetallic ores and these of the oxidation zone have been dumped as a two piles. The natural stream draining the waste piles has been transformed in acid mine drainage (AMD). The wastes have not been fixed and hence ravine’s swampy territory below the tailings piles have been covered with the derived waste matter. The interactions between the bog peat substances, AMD and wastes pore solutions have occurred for 50 years. It have been established the elements precipitation and concentration on peat substance. The Zn, Cu, Pb, Zn concentrations in peat samples are comparable to these in the wastes. The ore contained 4 ppm of Au. The contains of Au in waste covering the peat substance range from 0.2 to 1.7 ppm. It have been obtained that the concentrations of Au in the peat that is contacting with sulfide-bearing waste are 0.3-14.3 ppm. The Fe hydroxides, sulfides, jarosite, gypsum are established there.

The speciation of Au, Ag, Hg, Th and U in peat material has been determined using the selective extraction technique. It have been identified the following elements forms in peat substances: the water-soluble forms, these associated with organics/sulfides and with the Fe(III) hydroxides/oxides and residue. The part of all being studied elements is partially attributed to the water-soluble compounds (0.1 Au, 0.6 Hg, 0.08 Th, 0.5 U ppm). Gold is partly presented as organocomplexes ore sulfides (up to 1.4 ppm). In places where the gold concentration is in reaches 10 ppm, it appears mostly in the native form. The submicrometer gold Cu-bearing grains are observed among secondary minerals of Fe and are formed on the detrital material. Silver may enters as isomorphic admixture in the jarosite and mainly presents in contaminated peat as Fe(III) hydroxides/oxides fraction. Mercury as organocomplexes and/or as the secondary sulfide of Hg has been registered in peat samples. The major unit of U is associated with organic material and Th is with residual fraction.

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Organic and inorganic scCO₂-rock interactions – Results from laboratory experiments

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Mineralogical changes in the reservoir in the cause of CO₂ injection and its propagation may provide information on e.g. CO₂-induced geochemical interactions and are of great importance for the estimation of potential risks of geological CO₂ storage. To overcome the gap of direct observations, experimental studies at simulated reservoir conditions are an important tool to study all types of potential CO₂-fluid-rock interactions ex situ on mineral phases or real reservoir samples.

In this broad experimental study, our aim was to examine the role of supercritical CO₂ (scCO₂) on the mobilization of organic compounds from mineral phases as well as the changes in elemental and mineralogical composition of reservoir and cap rock samples due to the defined temporal exposure to scCO₂ under varying p-T-conditions. For this purpose several flow-through experiments using scCO₂ have been performed [1] on real rock samples of different lithologies from an real CO₂ storage site: the Ketzin site in Germany.

ScCO₂-extracts as well as untreated and scCO₂-treated rock samples were analysed using a variety of organic and inorganic geochemical, mineralogical and microscopic techniques to detect changes compared to untreated twin samples.

Generally, organic matter mobilization – mainly the low molecular weight organic acids formate and acetate - occurred linearly within the first 8 hours, then continued with decreasing extraction yields. XRD and XRF analyses revealed no quantitatively distinguishable changes in elemental and mineralogical composition between scCO₂-treated and untreated twin samples. However, SEM images indicated blastesis and corrosion effects on mineral surfaces as well as a partly loss / destruction of primary cements due to the exposure to scCO₂.

Re-Os constraints on gold mineralisation events in the Neoarchaean Storø supracrustal belt, Southern West Greenland

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The Storø supracrustal belt in Godthåbsfjord, southern West Greenland, hosts gold mineralization that is associated with arsenopyrite along a contact between lithological units and along the axial plane of a large fold core. Here we present new arsenopyrite Re-Os and zircon U-Pb data to constrain the age of the debated Storø gold deposit. Arsenopyrite from a stratiform mineralisation yield a 2.71 ±0.05 Ga isochron and model ages for highly radiogenic arsenopyrite form a bimodal distribution with peaks at 2.66 Ga and 2.71 Ga respectively. The older population combined with the isochron result yields a weighted mean of 2.707 ±0.008 Ga (MSWD = 0.57, n=4). A 2.64 ±0.02 Ga isochron from arsenopyrite from the axial plane of the fold core indicate a two-stage mineralisation process. The 2.64 ±0.02 Ga isochron is in perfect agreement with U-Pb zircon data (Nutman et al. 2007. Prec. Res. 159, 19-32), which are best explained by orogenic mineralisation during amphibolite facies metamorphism along structural weak planes. The initial 187Os/188Os value of 0.56 ±0.16 for the 2.64 ±0.02 Ga isochron indicates a crustal source for the metals, whereas the initial 187Os/188Os = -0.1 ±0.6 for the 2.71 ±0.05 Ga isochron remains unconstrained. Nevertheless, these data are best explained by relatively short crustal residence times of less than 0.1 Ga, wherein the Os, and associated metals, were extracted from the mantle after 2.8 Ga, and in which the 2.64 ±0.02 Ga stage formed by mobilisation of an earlier mineralisation around 2.72 Ga. Such a model is corroborated by detrital zircon constraints, which imply that volcanism and the first mineralisation stage is ≥2.8Ga. Finally, the ~2.63 Ga amphibolite facies metamorphic event in the Storø supracrustal belt was important for the redistribution of gold bearing sulphide minerals.

Marcasite in clastic sediments – Formative processes and deep time stability

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Marcasite occurs in marine and brackish water shale, claystone, and sandstone units from multiple locations and ages (Proterozoic through Eocene). Textural observations, such as differential compaction around marcasite concretions, indicate that these marcasites formed during early diagenesis in surface sediments. In marine shales and sandstones, textural studies suggest that marcasite precipitation is intimately associated with corrosion and destruction of frambooidal pyrite for the former, and with destruction of reworked early diagenetic pyrite concretions for the latter. Marcasite formation in association with pyrite destruction is consistent with a scenario whereby earlier formed diagenetic pyrite is re-oxidized in surface environments to produce the low-pH conditions required for marcasite formation.

In brackish water claystones, marcasite occurs as radial fibrous masses along the margins of burrows that penetrated into reducing sediments. Soil science research that associates marcasite formation with water-logged acid sulfate soils in coastal settings suggests that this marcasite as well formed because oxidation of pre-existing iron sulfides provided favorable conditions for marcasite growth.

Marcasite concretions from both marine and brackish water settings show multiple generations of marcasite growth, and δ34S values were measured from successive generations in micro-drilled samples and by ion-probe. The data show the lowered δ34S values indicative of microbial sulfate reduction in surface sediments, as well as a wide range of δ34S values suggestive of variable degrees of system closure (marine) and salinity fluctuations (brackish).

The studied samples range from approximately 50 million to 1.6 billion years in age and were all collected from unmetamophosed sediments. Marcasite is considered metastable and thought to invert to pyrite over time. Our observations indicate that this conversion proceeds very slowly at low temperatures (<200°C). In general, partial conversion of marcasite to pyrite is minor to absent for fine grained sediments (shales and claystones), and common and completed to various degrees in sandy sediments.
**High precision Ca isotope analysis using MC-ICPMS and TIMS**  

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 Calcium is a refractory lithophile element and a major rock-forming constituent of rocky planets. Whereas most Ca isotopes are synthesized during hydrostatic and explosive nucleosynthesis in massive stars, the synthesis of \(^{48}\)Ca is unique, as it is only efficiently produced in a low entropy environment most likely achieved in a type-Ia supernova [1]. Thus, high-precision Ca isotope measurements of meteorites and their components allow for a better understanding of the nature of the various stellar sources that contributed matter to the nascent solar system.

However, there are several challenges for the precise measurement of Ca isotopes. The natural abundance of the six stable isotopes (40, 42, 43, 44, 46 and 48) of Ca varies by a factor of >24000 (40 to 46), providing an obstacle for the simultaneous measurement of all Ca isotopes. In addition, there is a 20% mass difference between \(^{40}\)Ca and \(^{48}\)Ca, which produces a large mass dispersion beyond the geometry of either of the mass spectrometers used in our study. To overcome these issues we used a combination of TIMS and MC-ICPMS, where the low mass range (40-44) was measured using a Triton TIMS, while the overlapping high mass range (42-48) was measured using a Neptune MC-ICPMS. To precisely analyse \(^{48}\)Ca using the MC-ICPMS we measured in high-resolution (m/\(m\)! 6500) and at total beam intensities of >5000 V. To further avoid direct isobaric interferences from Ti and Sr, we also established an improved chemical separation of Ca effectively eliminating especially Ti and Sr.

Repeated analyses of rock standards relative to the NIST SRM915b Ca-standard demonstrate that our approach allows the measurement of \(^{40}\)Ca/\(^{44}\)Ca, \(^{42}\)Ca/\(^{44}\)Ca, \(^{43}\)Ca/\(^{44}\)Ca and \(^{46}\)Ca/\(^{44}\)Ca to 50, 2.5, 30 and 12 ppm (2 sd), respectively, when normalized to \(^{42}\)Ca/\(^{44}\)Ca. This represents a 100-fold improvement compared to previous studies for the less abundant isotopes of Ca. Using this improved resolution, we have re-investigated the extent of Ca-isotope heterogeneity in the solar protoplanetary disk by analyzing a suite of strategically-selected inner solar system objects.


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**Inhibition of calcite dissolution kinetics during direct liming of acid surface waters**  

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Dissolution kinetics of pure calcite is well investigated, e.g. [1, 2]. But, composition of natural carbonates, as well as the constituents in mine waters, have a strong influence on the solution kinetics and may inhibit dissolution processes during lake liming.

The reactivity of synthetic marble powder and industrial products was investigated. Significant differences in reactivity was obvious at p\(\text{CO}_2\) > 3.8 • 10\(^{-4}\) atm. Ions typical for acid mine drainage (e.g. Mn\(^{2+}\), Cd\(^{2+}\), SO\(_4\)\(^{2-}\)) do have different effects on the kinetic of carbonate dissolution. Manganese ions (c = 8.98 • 10\(^{-4}\) mmol/L) inhibit calcite dissolution. Experiments with 5-times excess of calcite results in 66.4% of dissolved calcium compared to experiments without inhibitor. Providing a surplus of calcite particles (20-times excess) results in 92.7% of the equilibrium concentration and a significant time-shift in reaching equilibrium (20,000 min instead of 12,000 min).

Cadmium has as well a significant influence on dissolution and kinetics. Only 58.2% of the calcium concentration was reached with cadmium as inhibitor (c = 7.65 • 10\(^{-6}\) mmol/L) compared to the dissolution in pure water. Using carbonate 20 times in excess revealed a slightly higher dissolution reaction (63.8%).

Increased CO\(_2\) partial pressure might be used to compensate inhibition by material impurities and/or water constituents.

The microbiology and biogeochemistry of sulfidic mine dumps
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The microbiology and the relevant biogeochemical processes in the dumps and heaps are reviewed and have to be understood for improving copper heap leaching operations and to develop and control countermeasures for the formation of acid mine drainage (AMD). Pyrite or pyrrhotite oxidation is the most relevant biogeochemical process in sulfidic mine waste dumps and heaps and different techniques have been applied to measure reaction rates: column experiments, humidity cells, heat flow measurements, or oxygen consumption measurements. Acidophilic Fe(II)- and sulfur-oxidizing microorganisms are most relevant for metal sulfide oxidation. Anaerobic biogeochemical processes in sulfidic mine dumps and heaps are Fe(III)- and sulfate reduction, but little is known about the reaction rates. Fe(III)-reducing microorganisms dissolve Fe(III)(hydr)oxides and may thereby release adsorbed or precipitated metals. Sulfate-reducing microorganisms precipitate and immobilize many metals. Mainly culturing approaches were used to study the microbial communities in sulfidic mine dumps and heaps. More recently, molecular biological techniques have been applied to investigate the microbial diversity and to quantify and monitor particular microorganisms.


Bioremediation strategies to inhibit salt-enhanced stone weathering
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Salt weathering is an important mechanism contributing to the degradation and loss of carved stone and historic stone buildings. Stone monuments in the presence of salt and water, suffer from salt-enhanced physical and chemical weathering. It has been observed that weathering rates of rocks in nature, as well as building stones, are slowed down by naturally occurring or artificially produced patinas. These tend to be bacterially produced, durable mineralized coatings that lend some degree of protection to the underlying stone surface [1].

Our research shows that bacterially produced carbonate coatings can be quite effective at reducing both physical and chemical weathering of stone by soluble salts. The calcite-producing bacteria used in this study were isolated from stone monuments in Granada, Spain [2] and cultivated in an organic-rich culture medium on a variety of artificial and natural substrates (including limestone, marble, sandstone, quartz, calcite single crystals, glass cover-slips, and sintered porous glass). Scanning electron microscopy (FESEM) was used to image bacterial calcite growth and biofilm formation. In situ atomic force microscopy (AFM) enabled calculation of dissolution rates of untreated and treated surfaces. 2D-XRD showed the mineralogy and crystallographic orientation of bacterial calcium carbonate. Results indicate that bacterially produced calcite crystals form a coherent, mechanically resistant surface layer in perfect crystallographic continuity with the calcite substrate (self-epitaxy). These calcite biominerals are more resistant to chemical weathering by salt-enhanced dissolution, apparently due to the incorporation of organics (bacterial exopolymERIC substances, EPS). Conversely, on silicate substrates, non-oriented vaterite forms, leading to limited protection. Organic films formed on treated substrates appear to promote salt crystallization at reduced supersaturation [3], thus reducing salt crystallization pressure and minimizing physical damage. These preliminary results indicate that bacterial treatments have tremendous potential to protect built cultural heritage.

Mineral assemblages and metamorphic history of granulites in the Rychleby Mts., Bohemian Massif

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Relics of high-pressure metamorphic rocks are preserved in various crustal and mantle segments of the Variscan orogen in central Europe. These rocks may provide important insights into early stages of plate convergence and burial as well as exhumation mechanisms. We use mineral assemblages and chemistry to reconstruct the pressure-temperature (P-T) paths of high-pressure granulites in the Rychleby Mts., Bohemian Massif. Mafic granulites consist of garnet, omphacite, kyanite, two feldspars, and quartz with accessory rutile and zircon. The peak assemblage was partly replaced by paragentic amphibole and biotite during exhumation. Garnet grains are zoned from Gr₃₆Py₁₀Alm₅₄ (core) to Gr₁₅Py₃₈Alm₴₂ (rim), and host inclusions of phengite, omphacite, unmixed feldspars, kyanite, and rutile. Omphacite composition varies from Di₄₄Hd₁₄Jd₄₂ (inclusions of phengite, omphacite, unmixed feldspars, kyanite, and rutile). Garnet preserves zoning from Gr₃₂Py₁₀Alm₆₈ (core) to Gr₂₀Py₃₈Alm₴₂ (rim), and host inclusions of phengite, garnet, kyanite, quartz, and biotite during exhumation. Garnet grains are zoned from Gr₃₆Py₁₀Alm₅₄ (core) to Gr₁₅Py₃₈Alm₴₂ (rim), and host inclusions of phengite, garnet, kyanite, quartz, accessory rutile, and zircon. Garnet preserves zoning from Gr₃₆Py₁₀Alm₅₄ (core) to Gr₁₅Py₃₈Alm₴₂ (rim), and it contains inclusions of phengite, sometimes replaced by biotite and zoisite. We have applied infrared (µFTIR) spectroscopy. Micro FTIR maps of single hyphae at a micrometer scale using Confocal Laser Scanning Microscopy (CSLM) and synchrotron based micro Fourier Transform Infrared (µFTIR) spectroscopy.

Biochemical characterization of single weathering hyphae of Paxillus involutus using CLSM and synchrotron based µFTIR

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The mycelium of symbiotic ectomycorrhizal fungi (EM) increases nutrient uptake by the plants through fungal secretion of low molecular weight organic acids that can accelerate mineral dissolution. This EM weathering with pine trees plays a key role in nutrient mobilization processes and pedogenesis. Here we report first insights into the chemical variability of the weathering mycelium when studied on a micrometer scale using Confocal Laser Scanning Microscopy (CSLM) and synchrotron based micro Fourier Transform Infrared (µFTIR) spectroscopy. Pine seedlings ectomycorrhizal with Paxillus involutus were grown in microcosms containing wells with olivine, quartz, basalt, granite and limestone. CLSM analysis of EM hyphae with the molecular probe SNARF4F in contact with basalt and limestone revealed a pH below or at 4.6 while the pH of EM in contact with granite identified pH values that varied from pH 4.6 to 6.5 with variations observed within single cells. Chemical µFTIR maps of single hyphae at a resolution of 5x5 µm identified variabilities within the spatial distribution of lipids, amides and carbohydrates. Particular distinctions in intensities of carbohydrates and lipids were discovered on a single cell level.

We conclude that mineralogy has a significant impact on the biochemistry of colonizing symbiotic EM mycelia, individual hyphae and cells. Earlier studies showed that exudation of oxalate is increased in the presence of basalt and limestone[1] and here we report the corresponding biochemical changes that take place on a single hypha scale.

Growth- and post-growth behavior of major and trace elements in garnets, a case study

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The distribution of major and trace elements in the mineral garnet plays an important role in the interpretation of ages deduced by e.g. Lu-Hf and Sm-Nd garnet geochronology. A common understanding is that Lu and other heavy rare earth elements (HREE) have high partition coefficients for garnet, hence will be enriched in early formed garnet cores, while on the other hand light rare earth elements (LREE), such as Sm, will be incorporated during late growth into garnet rims. Further, distribution patterns of HREE in garnet are important indicators for processes during metamorphism as they might point to episodic and multi-generation garnet growth, as well as to mineral reactions producing distinct enrichment peaks during garnet growth (e.g. amphibole- & epidote-out reactions).

In this study we investigate these distribution patterns of major and trace elements in a variety of garnets from chemically different host rocks, and discuss the influence of e.g. diffusion on the preservation of growth zoning.

The first results show that nearly all single-generation garnets indeed preserve element distribution profiles with an enrichment of Lu and other HREE in garnet cores. Interestingly diffusion often seems to play a negligible role for the HREE compared to the major elements. Distinct Lu peaks in garnet cores do on the one hand correspond to well-preserved Mn peaks, but also Lu enrichments together with flat Mn patterns are observed, which indicates that Lu (and presumably other HREE) are less prone to diffusional resetting compared to e.g. the major elements. One of the major aims of this study will be to constrain how explicitly diffusion can influence and alter major and trace element distribution profiles in garnets and how these are interrelated with each other. With this information it hopefully will be non-ambiguous to interpret geochronological data of garnets from the Lu-Hf and Sm-Nd isotope systems.

Role of fluid flow conditions on denitrification rates in sediments during managed groundwater recharge

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We measured in situ denitrification during infiltration through saturated sediments to develop a mechanistic understanding of controls on denitrification rates. Sampling and measurements were completed below a managed aquifer recharge pond, providing strong constraints on initial nitrate and carbon concentrations, flow rates, and other controlling parameters. Co-located thermal measurements were used to determine flow rates with time, and chemical and isotopic methods were used to assess denitrification progress. Zero order denitrification rates of 3 to 300 µmol L⁻¹ d⁻¹ were measured during infiltration. Denitrification was not detected at times and locations where the infiltration rate exceeded a threshold of approximately 0.9 m d⁻¹. Pore water profiles of oxygen and nitrate concentrations indicated a deepening of the redoxcline at higher flow rates, which reduced the thickness of the zone favorable for denitrification. Below the threshold infiltration rate, denitrification rates were positively correlated with infiltration rates, suggesting that for a given set of sediment characteristics an optimal range in infiltration rate exists for achieving maximum nitrate load reduction. This study has implications for managing water resources to achieve the greatest possible nitrate load reduction by denitrification in both natural and manipulated settings including recharge ponds, wetlands, and hyporheic zones in streams.
Zircon as a Raman spectroscopic pressure sensor

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Experiments using diamond-anvil cells have been crucial in understanding minerals and fluids at high pressure (P) and temperature (T) because sample properties can be studied in situ. Pressure in these cells must be determined indirectly, e.g. from the shift in wavenumber of a Raman line of a phase inside the sample chamber. The 464 cm⁻¹ Raman line of quartz has frequently been applied as pressure sensor because of its fairly large shift with P (δν/δP ~ 9 cm⁻¹/GPa) and relatively small shift with T (δν/δT ~ 0.014 cm⁻¹/K) [1]. However, its use is limited by phase transitions and high solubility of quartz in many fluids and melts. In such situations, zircon represents an option because it is stable over a larger range in P, T, and fluid composition (e.g. [2]).

In this study, we calibrate the shifts in wavenumber of the ν₂-SiO₄ (~1008 cm⁻¹) Raman band of fully crystalline synthetic zircon with T and P. The relationship between wavenumber and T from 22 to 950 °C is described by the equation ν (cm⁻¹) = 7.26*10⁵ T (°C) - 1.58*10³ T (°C)² - 2.893*10⁻² T (°C) + 1008.64. At ~25 °C, the δν/δT slope to 6.6 GPa is 5.69 cm⁻¹/GPa, and that to 2 GPa is 5.81 cm⁻¹/GPa. The latter does not significantly change with temperature, as determined using a Bassett-type hydrothermal diamond-anvil cell [3], with the pressure based on the EoS of H₂O [4]. The observed δν/δP slopes are 5.88 cm⁻¹/GPa for the 700 and 600 °C isothersms, and 6.08 cm⁻¹/GPa along the 500 °C isotherm. The zircon pressure sensor was used to obtain isochores for these isochores were at significantly higher pressures (by up to ~700 MPa) than calculated from the liquid-vapor accumulation of the crusts is required. Here we report on the distribution of the geochemical twin elements Zr-Hf and Nb-Ta in ferromanganese crusts from the Northern and Southern Central Pacific, the Eastern North Atlantic and from the hydrothermal vent field Logatchev-1. Recent studies [e.g. 1] dealing with the distribution of Zr-Hf and Nb-Ta in the Pacific Ocean show a fractionation of these elements relative to chondritic values throughout the water column, with distinct signatures in different water masses. Our investigated depth profiles of ferromanganese crusts cover up to 20 Ma and are characterized by highly variable distributions of Zr, Hf, Nb, and Ta, accompanied by changing and fractionated Zr/Hf and Nb/Ta ratios. The Zr/Hf ratios in crust surfaces are always lower compared to the range of Zr/Hf ratios in modern deep seawater. Thus, ferromanganese crusts do not inherit the Zr/Hf (and Nb/Ta) signature of the water mass at the location of crust formation and the ratios cannot be used as paleoceanographic tracers. The elements are almost exclusively bound to the Fe oxyhydroxide fraction of the crust and are probably enriched via surface precipitation. While the Fe oxyhydroxide colloids and particles accumulating in the crusts may have formed away from the crust location and would then carry a different, integrated signal [2], the always lower than seawater Zr/Hf ratios in the crusts also indicate the preferred enrichment of Hf relative to Zr during accumulation in the crust and thus a fractionation of the dissolved seawater Zr/Hf ratio. Seawater data for Nb-Ta are scarce, but a preferential enrichment of Nb in the Fe-Mn crusts can be suggested. The different particle reactivity of the geochemical twin elements is related to the different electron structure causing differences in complex stabilities and the type of chemical bonding. Further, the contribution of hydrothermal Hf to the marine Hf budget will be discussed.

Centennial-scale sea surface temperature and salinity change in the Florida Straits during the early Holocene

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Previous studies showed that sea surface salinity (SSS) in the Florida Straits [1] as well as Florida Current transport [2] covaried with changes in North Atlantic climate over the past two millennia. However, little is known about earlier Holocene variability in the Florida Straits. Here, we combine Mg/Ca-paleothermometry and stable oxygen isotope measurements on the planktonic foraminifera G. ruber (white variety) from Florida Straits sediment core KNR166-2 JPC51 (24° 24.70′N, 83° 13.14′W, 198m deep) to reconstruct a high-resolution (~35 yr/sample) early to mid Holocene record of sea surface temperature and δ18O_8water (δ18Osw, a proxy for SSS) variability. In addition, we also measured Ba/Ca ratios in the same shell material as a proxy for riverine input into the Gulf of Mexico over the same time interval. After removing the influence of global δ18Osw change due to continental ice volume variability, our δ18Osw record suggests early Holocene surface salinity enrichments caused by increased evaporation/precipitation ratios in the Florida Straits associated with periods of reduced solar output [3], increased ice rafted debris in the North Atlantic [4] and the development of more permanent El Niño conditions in the eastern equatorial Pacific [5]. When considered with previous high-resolution reconstructions of early Holocene tropical atmospheric circulation changes, our results provide evidence that solar output variability over the Holocene can have a significant impact on the global tropical hydrologic cycle.


Rare earth element variation in hydrothermal Fe-oxide Cu-Au systems

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Mineral deposits of Cu-sulphides and gold paragenetically associated with haematite and magnetite may also contain variable, in some cases economic levels of uranium and rare earth elements. The size of these deposits, e.g. Olympic Dam with an ore body in excess of 3x5x2km implies large, crustal scale fluid processes. Alteration of the host rock of these deposits is variable but distinct alteration mineral facies can be distinguished. The commonly identified regional geochemical footprint of these REE anomalous deposits is a pronounced sodic alteration (albitisation) with accompanying formation of calc-silicate / magnetite / Fe- amphibole breccias and metasomatism. On the depositional side of the mineralising system we can distinguish two types of alteration associated with Cu and Au mineralisation: i) a pyrite/magnetite dominated assemblage with pronounced potassic (biotite, K-spar) alteration and a predominance of chalcopyrite ± bornite, locally and variably overprinted by hematite + bornite + covellite + chalcocite. ii) a hematite dominated assemblage with bornite + covellite + chalcocite and much less chalcopyrite. Gold content appears related to sulphide abundance but Au rich zones with low sulphide grades are present. The different alteration/mineralisation zones have distinct REE patterns. The regional albitionisation zone, which is seen as the source region of the metal components displays a path of initial depletion of LREE followed by an overall REE depletion as the involved rock is progressively converted to an albitite. Intermediate sections dominated by magnetite / biotite / K-spar alteration can have intense enrichment of REE including the formation of discrete RE minerals (allanite) but this appears to be most related to a late stage of the mineralising process. A pronounced enrichment of the REE occurs in the hematite / sericite dominated section, with REE rich barite and fluorite as well as RE minerals such as bastnaesite, florencite, monazite and xenotime. On the mineral grain scale enrichment of REE and U is pronounced in the hematite / sericite dominated part of the system.
Growth rate effect on Sr/Ca and Mg/Ca partitioning between calcite and fluid: In situ data

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Sr/Ca and Mg/Ca (Me/Ca) abundances in speleothems, foraminifera, coccolith, and mollusks have been extensively used as paleotemperature proxies. However, inconsistencies exist between different Me/Ca-temperature calibrations which imply disequilibrium exchange of Sr/Ca and Mg/Ca between fluid and calcite, thereby jeopardizing their use as paleoclimatic proxies unless the overriding physico-chemical and biological effects on elemental partitioning can be calibrated.

This study complements existing experimental data on Sr and Mg partitioning that are mostly based on bulk analysis of calcite precipitated at different rates. In our alternative approach, the advancing rate of the crystal surface was determined by sequentially spiking calcite-precipitating fluids with rare earth element (REE) dopants. In situ secondary ion mass spectrometry (SIMS) analyses of Me/Ca were performed on single crystals of experimentally grown calcite at relative external reproducibilities for both ratios of ~1 % (1s.d.). REE patterns reveal concentric domains of calcite growth. The growth rate of calcite generally decreases with time - i.e. crystal rims advanced at slower rates than cores. Fluids were sampled periodically for Me/Ca, dissolved inorganic carbon, and pH.

SIMS profiles across individual calcite crystals displayed depleted Sr/Ca and elevated Mg/Ca at crystal rims relative to interiors. The partition coefficient of Sr/Ca (KdSr/Ca) increases by ~100±2% with increasing growth rate over the range of 1 to 8 µm/day (at 25°C). In contrast, KdMg/Ca decreases by ~33±16% over the same range.

Our results suggest that Sr (Mg) are enriched (depleted) in the near-surface region of calcite relative to the bulk crystal lattice. This observation is consistent with previous in situ data and the surface entrapment model [1, 2], which underscores that Sr/Ca and probably Mg/Ca in natural carbonates are not a direct proxy for marine and terrestrial temperature, and require corrections for the dependency of partitioning behavior on crystal growth rate.


Zircon rim response to metamorphic and hydrothermal regime-change

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A significant advance in zircon geochronology is the recognition of different types of neoblastic growth and recrystallization during tectonism and mineral-fluid interaction. Such domains can form in zircon and other accessory minerals as a consequence of alteration and dissolution-precipitation processes across a range of P-T conditions, and as low as ~200 °C particularly when in the presence of fluids. Distinct chemical and isotopic signatures associated with these alteration regimes can reveal valuable geological information regarding the timing and source of fluid influx, as well as mineral-fluid interaction at the sub-grain level. Application of SIMS depth-profiling now permit unparalleled spatial resolution analysis (down to ~0.2 µm) of these thin alteration zones. Complementary LA-ICPMS depth-profiling allows detection of geochemical changes accurately down to ~5 µm. Depth-profiling of unpolished zircon or other accessory crystal species measures changes in radiogenic (U-Pb), stable isotopic (δ18O) and chemical (REE) signatures that translate into concentration-depth profiles as drilling progresses into the crystal’s interior. One application is to resolve the source and timing of fluid-flow responsible for lode Au deposits of the Canadian Abitibi Province. Depth-profiling techniques successfully uncovered <3 µm alteration domains in wall-rock zircon, occurring as light REE-enriched “rims”, and Th/U and 18O values suggest that alteration involved limited crustal recycling. Zircon rim ages are significantly younger than host rock ages, and correlate to intensely mineralized and deformed quartz-carbonate-Au shear veins. Subsequent zircon alteration correlating to thin, shallow-dipping and less altered and mineralized vein networks occurred 20 m.y. later, and represents a late hydrothermal fluid pulse at the end of retrograde metamorphism. A similar approach revealed an episode of Eocene metamorphism (metasomatism?) in the western Cyclades of the Aegean, an area known for iron- and sulfide-ore skarn deposits. A dominant zircon population had a spongy structure created by complete recrystallization of the pre-existing crystal, possessing low Th/U and flat and depleted HREE patterns, and yielding Eocene ages with δ18O ~7‰. Detailed pre- and post-analytical imaging is necessary to document crystal structures and mineral outgrowths. Depth-profiling on zircon is a successful, yet nascent application for the dating of mineral deposits and fluid flow.
A multi-component reactive transport model assessment of microbial processes and trace metal cycling across a gradient in sulfate reduction rates along the California Margin
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Sediments and pore water from 4 ODP Leg 167 sites along the California Margin (1011, 1017, 1018 and 1020) were used to compare biogeochemical processes across a gradient of sulfate reduction (SR) rates with the purpose of studying the processes that control these rates and how they affect trace metal redistribution. Measurements of the trace element composition of pore water and sediment along with %CaCO3, %biogenic silica, wt% carbon and δ13C of Total Organic Carbon (TOC) were used to constrain the multicomponent reactive transport model CrunchFlow. The rates of sulfate reduction, methanogenesis and anaerobic methane oxygenation (AMO) were constrained by fitting the model to the measured concentration profiles. The sites are distinguished by the depth of AMO: a shallow zone is observed at sites 1018 (14 to 19 mcd) and 1017 (23 to 27 mcd), while deeper zones occur at sites 1011 (45 to 55 mcd) and 1020 (97 to 113 mcd). In general, the sulfate reduction rates are faster (on the order of 9-9.9x10^-17 mol/L/yr) for the shallow zones, compared to 1-1.4x10^-17 mol/L/yr for the deeper zones. AMO rates are also faster at the shallow belt 2x10^-7 mol/L/yr compared to 3x10^-8 mol/L/yr at the deeper sites. Sites with shallow sulfate reduction zones appear to have high rates of AMO resulting in high alkalinity concentrations close to the sediment-water interface. The dissolved metal ion concentrations also varied between the sites, with Fe (0.01-7uM) and Mn (0.01-57uM) concentrations highest at Site 1020 (water depth 3000m) and lowest at site 1017 (water depth 950m). The highest Fe and Mn concentrations occurred at various depths, with no direct correlation to sulfate reduction and alkalinity maximum values. Modeling of the dissolved and solid SiO2, Ca, Mg, K, Mn and Fe is used to establish the relationship between the biogeochemical reactions and trace metal variations and to better constrain the parameters that influence the trace metal distributions in the sediment column.

Dissolved reactive mangenate at pelagic redoxclines
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Experiments with suboxic freshwater and seawater suggest a dissolved reactive manganese fraction (dMnreact) that completely oxidizes within 36 h, mainly by microbial activity. The fast redox cycle of Mn drives the ‘Mn pump’ transporting metals into anoxic basins. A difference method can be used to determine dMnreact. One aliquot of a water sample is directly filtered and represents the total dissolved Mn. A second aliquot is aged under atmospheric oxygen and app. 20°C and filtered after 36 h representing the residual dissolved Mn(II). The concentration of dMnreact is calculated as difference of both aliquots.

Application to the Black Sea revealed dMnreact profiles comparable to published Mn(III) patterns analysed with a polarographic method. Both methods show that the upper part of the suboxic zone consists exclusively of dMnreact or Mn(III). dMnreact is a half quantitative measure of dissolved M(III), an unknown fraction of i) autocatalytic oxidation of dissolved Mn(II) by readily produced MnOx and ii) microbial Mn(II) oxidation. Thus, the present method helps to assess the full potential for oxidation of dissolved Mn within an aquatic environment. The method has the advantage that sample preparation can be easily done on site, followed by analysis of dissolved Mn by conventional methods in the lab.

dMnreact was also detected in the Landsort Deep (Baltic Sea) with values distinctly increasing from the outer regions towards the central part (max. 3 µM). Similar to the Black Sea, dMnreact concentrations increase in the suboxic transition zone separating oxygenated and H2S containing waters. In contrast, almost no dMnreact was present in the Gotland Basin (Baltic Sea). Pronounced lateral currents and turbulence in the Gotland Basin prevent the formation of a stable suboxic zone, a prerequisite necessary for accumulation of dMnreact. Such intrusions supply trace amounts of O2 and H2S thus causing either immediate oxidation/reduction of dMnreact or deterioration of its stabilising ligands.

Analysis of dMnreact in the seasonally anoxic Lake Dagow (Germany) revealed maximal concentration of 6 µM. This value significantly exceeds the level of the Landsort Deep most likely due to the stable stratification of this lake during sampling.
Decoupled evolution of temperature and precipitation in Western Germany during the Last Interglacial reconstructed from a precisely dated speleothem

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We present high-resolution δ18O, δ13C and trace element profiles for stalagmite HBSH-1 from Hüttenbläserschacht-höhle, western Germany. The major part of the sample grew between 130 and 80 ka providing a climate record with decadal to centennial resolution for Marine Isotope Stage (MIS) 5. The record shows three growth interruptions during this period coinciding with the Greenland Stadials suggesting that stalagmite growth in this area is a very sensitive proxy for cool and dry conditions in the northern hemisphere.

We interpret stalagmite δ18O as a proxy for past temperature changes, whereas stalagmite δ13C rather reflects changes in the hydrologic balance. The δ13C record shows three pronounced negative peaks during MIS 5, and the timing of those is in agreement with MIS 5e, 5c and 5a. This suggests warm and relatively humid climate in western Germany for these phases.

During the Last Interglacial, the evolution of δ18O and δ13C is opposite. Whereas the δ18O signal suggests the warmest conditions around 125 ka followed by a gradual decrease, the δ13C signal indicates wetter conditions towards the end of the Last Interglacial. This ‘decoupling’ of temperature and humidity during MIS 5e is also visible in a series of snapshot simulations performed using the general circulation model FAMOUS. The decoupling is probably related to the change in solar insolation, which influences the atmospheric dynamics and storm activity in the region.

Mumia vera – vera mumia?

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The drug mumia vera has a long tradition not only in Arabian but also in ancient European medicine. The knowledge in antiquity of the curativeness of asphalt combined with the belief in the magics of death made mumia vera a precious ingredient of medications with a very broad spectrum of indications. Since the 16th century it was even used as paint pigment. The export of mummies is supposed to have started in the 12th century and the drug was still available in 1924. Because the export of mummies was banned by the Arabs since the 17th century a more or less macabre market of substitutes developed.

![Figure 1](image)

A small amount of ground mumia vera from a pharmaceutical vessel of the early 18th century was analysed on a molecular level. A number of diverse particles were hand-picked under the microscope and analysed separately via CP-pyrolysis GC-MS. Extracts were analysed by GC-MS. The ingredients of all particles exhibited a close relation to authentic ancient mummy material and published data in this field [1, 2, 3]. Besides fibres of linen and wood as well as embalming material (cedrium, pistacia turpentine, beeswax, Dead Sea asphalt) pieces of most probably human tissue and a wax-like substance (possibly a kind of adipocere) were found. Some inconsistencies in the data point to a mixture of material most plausibly due to occasional refilling of the vessel. Genuine mummy material milled as a whole obviously was used as medicine in the present case.

Experimental constraints on Ag isotope fractionation during planetary core formation

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A recent study [1] proposes a heterogeneous accretion scenario for the Earth, which is for the first time based on isotopic constraints from the short-lived Pd-Ag, Mn-Cr and Hf-W decay systems. The study concludes that the Earth inherited the major part of its moderately volatile element depletion from its building blocks. The model also requires a late addition of volatile-rich material while core formation was still active. These findings are in good agreement with work based on elemental abundances of the BSE (Bulk Silicate Earth) and partitioning experiments (e.g. [2]) as well as dynamic models of the accretion and planet formation [3]. The late addition of volatile-rich material is mainly required by the Pd-Ag decay system to explain the identical Ag isotope compositions but different Pd/Ag ratios of CI chondrites and BSE.

The need for a late volatile-rich addition can be relaxed by proposing that the true BSE Ag isotope composition is more radiogenic (~ +1.2 epsilon107Ag/109Ag) than the measured value (~ -2.2 ± 0.7 [1]), because the latter was modified by extraction of light Ag into the Earth’s core. To explore this possibility, we performed experiments on mixtures of silicate, sulphide and metal in a piston-cylinder apparatus at 1.5 GPa and 1800 K. Metal and silicate phases of the run products were manually extracted and analysed for Ag isotopes on a MC-ICPMS following the protocol of [4]. The Ag isotope compositions obtained for metal and silicates were identical within the analytical uncertainty (± 0.5 epsilon). This demonstrates that Ag isotope fractionation is negligible at the investigated conditions. Isotope fractionation generally decreases with T -2 at the temperature range considered for metal-silicate equilibration in a deep magma ocean. Therefore it is likely that Ag isotopes do not fractionate at conditions predicted for terrestrial core formation (higher T and P). Moreover, the experimental results also show that Ag partitioning into the metal increases with sulphur content.


Evidence of mantle heterogeneity underneath slow-spreading ridges?
Case study at 45°N mid-Atlantic ridge

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Axial volcanic ridges (AVR) are a ubiquitous feature along mid-oceanic ridges. Although numerous studies have been performed on their structure and volcanic activity, many questions still remain unanswered, e.g. do AVR basalts have a common parental magma, and are the basalts derived from different magma chambers erupting at different times?

During cruise JC24 in 2008, nearly 300 basaltic samples were collected with the ROV ISIS in order to answer some of these questions.

A large dataset has now been compiled and some preliminary results will be presented. Rare earth element (REE) data coupled with trace element data of 30 samples revealed three different groups of samples. Group I is characterized by low La/Yb, incompatible element concentrations between normal and enriched mid-oceanic ridge basalt (N- and E-MORB). Group III has highly elevated La/Yb ratios, and a pattern of incompatibles that is more enriched in light REE than E-MORB. Group II lies in between but shows clear gaps to both other groups.

As REEs are not available for all samples yet, the incompatible and alteration-resistant elements Nb-Zr-Y were used to extend the grouping to a further 230 samples analysed by XRF. The results are coherent with the REE groupings. In addition, groups II and III could be subsequently split into subgroups.

The most enriched samples occur on (1) flat-topped volcanoes, situated off-AVR, (2) in the median valley near these volcanoes, (3) in the median valley walls on the western side as well as in the western axial floor, and (4) at the northern tip of the main AVR structure. Group II occurs on the axial floor north and west of the AVR, in the western median valley wall, and at the northern and southern tips of the AVR.

It is the aim of this study to reveal connections between volcanic structures, as well as to define the various melt sources.

Wider implications of this study are insights into the magma storage and plumbing underneath the AVR, and a detailed geochemical map of a (typical) mid-Atlantic ridge segment.
Lessons to learn from amino acid distribution in POM of Lake Baikal

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Lake Baikal offers a unique opportunity to study water column processes in a freshwater system with conditions similar to oceanic systems. With a maximum water depth of ~1640 m, Lake Baikal is the deepest lake on Earth and due to efficient vertical mixing, oxygen concentrations are high throughout the water column.

Furthermore, although Lake Baikal receives considerable input of suspended particles via rivers, primary production in the surface waters is the major source of carbon and energy for organisms in deeper water layers and in the sediments. Sediment trap material from Lake Baikal, collected at 18 different water depths (50-1350 m), has been investigated for total hydrolysable amino acids (THAA) and amino acid D- and L-enantiomers. The THAA flux decreased by 50% in the upper 500 m and remained constant below this depth, indicating that organic matter (OM) degradation was mostly restricted to the upper water column.

We additionally measured nitrogen isotopes on THAA (POM) from different water depths that allowed for determination of source and food web changes.

The dependence of $^{222}$Rn air-water partitioning on water temperature and water salinity

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Radon ($^{222}$Rn) is used as natural aquatic tracer for many applications. A prominent example is its use as indicator for submarine groundwater discharge (SGD) processes. On-site radon-in-water detection is performed by means of a mobile radon-in-gas monitor and radon extraction from the water into a closed circulating air volume. For converting the detected radon-in-air concentration into radon-in-water values the water/air partition coefficient ($K_{w/air}$) needs to be known.

$K_{w/air}$ depends on two water parameters that are easily attainable on site: temperature and salinity. Possible values for $K_{w/air}$ cover a range between about 0.50 (cold fresh water) and 0.03 (hot saline water). The temperature dependence of $K_{w/air}$ applies for all environments (terrestrial and marine) and is generally taken into consideration. The ‘salting out’ of radon, however, is often underestimated or not accounted for at all, potentially leading to an erroneous data interpretation.

Theoretical considerations that are based on reported data as well as on an extensive own dataset resulted in the easily applicable equation shown below. The equation allows for uncomplicated consideration of the dependence of $K_{w/air}$ on both, temperature ($T$ [K]) and salinity ($S$ [‰]) (see Fig. 1).

\[
\ln \beta = -55.90 + 92.49 \left( \frac{T}{100} \right) - 22.24 \left( \frac{T}{100} \right) + 2\left[ -0.219 \times 0.138 \left( \frac{T}{100} \right) - 0.022 \left( \frac{T}{100} \right) \right]
\]

Figure 1: Dependence of the air/water partitioning coefficient ($K_{w/air}$) of radon on water temperature and salinity (cf. Eq. 1)
Exploring micro-scale stable isotope variations using femtosecond laser ablation MC-ICP-MS

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We present advancements in micro-scale analyses of non-traditional stable isotopes using a second generation custom build femtosecond laser ablation system coupled to a multicollector ICP mass spectrometer.

The heart of our laser ablation system is based on the latest generation Ti-Sapphire regenerative amplifier system Spectra Physics Solstice, which produces 100 fs infrared (IR) laser pulses with up to 3.7 mJ/pulse. Non-linear optics are used to convert the fundamental IR wavelength into the UV with a wavelength of 196 nm and an adjustable pulse energy of up to 0.1 mJ/pulse. The system provides full control on laser parameters, such as spot size, energy density, pulse width, repetition rate (continuous from 1 to 1000 Hz) and beam shape. The spot size can be varied from 10 to 100 µm in diameter with energy densities on the sample between 0.1 and 50 J/cm².

The laser beam is delivered to the sample (thin sections or polished blocks contained in a He-flushed sample cell) through a fully automated and computer controlled microscope stage, modified with UV optical components to focus the laser beam and visualise the sample surface. Special emphasis in the construction was given to high quality optical imaging of the sample, while maintaining an optimum laser beam quality.

A custom-designed software allows integrated control on laser parameters, sample positioning and observation, as well as fully automated analyses through a synchronised operation with a Thermo Neptune MC-ICP-MS, equipped with a Neptune Plus Jet Interface for increased sensitivity.

We will present results on optimized analytical conditions for stable isotopes measurements of Fe, Si, and Mg at the micro scale in various matrices, such as minerals, glasses, and soils.

Climate change and the KISS principle

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Mineral carbonation is the logical answer to rising CO₂ levels. The CO₂ is captured in a safe and sustainable way and returned to the rock record as solid carbonates. The recipe is simple and straightforward:

- select an abundant material that weathers easily (olivine or serpentine)
- mine and mill this material
- spread it in a favorable climate for weathering

Instead of leaving it at that, and follow the KISS principle (Keep It Simple, Stupid), most researchers try to develop techniques to speed up the carbonation. This costs extra energy and money. This is a major reason why the storage of CO₂ in abandoned oil and gas fields, or in saline aquifers is still the favored mitigation strategy. Mineral carbonation has been overlooked, mainly because researchers have made it too complicated in their attempts to speed up the reaction.

There is no need to speed up the reaction, as olivine grains of 100 µm weather and capture CO₂ in a few years in a suitable climate. Extrapolation of abiotic experiments suggests that weathering is not fast enough. Outside the laboratory the role of biotic factors like mycorrhizal fungi on land or lugworms on tidal flats has been demonstrated, which speed up the weathering reaction by factors of ten to almost one thousand. Crushed serpentinite mine tailings in British Columbia are known to weather fifty times faster than basaltic tuffs in even the most favorable climate for weathering.

For the global C-cycle it makes no difference where the CO₂ is captured, as the atmosphere is a well mixed reservoir on the timescale of a few months. Capturing and storing of CO₂ from flue gases is too expensive. The separation step alone costs already considerably more than straightforward enhanced weathering.

The strategy for enhanced weathering relies upon olivine mined in the wet tropics. This material is milled and the grains are spread over the surrounding area. The whole operation (mining, milling and transport) will cost around 10 Euro/ton of captured CO₂. Negative effects on the environment are unlikely.
**Nanocalcite as a model for biogenic, geological calcite**

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Many geological systems, including chalk, limestone, and calcareous sandstone, contain sub-µm (nano), biogenic calcite formed by organisms long ago. These systems are intimately linked to environmental and economic interests (e.g. aquifers and petroleum reservoirs). Many geochemical research studies seek to understand the transformation (e.g. growth/dissolution) and reactive influence of calcite on pore fluids. For model system calcite, studies typically use commercial samples or calcite synthesized from super-saturated solutions of Ca²⁺ and CO₃²⁻. The particle size of these types is generally much larger than biogenic calcite, and industrial calcite often contains trace amounts of the chemicals used during the manufacturing process or for ensuring good storage properties.

We explored an alternative method for synthesizing nanocalcite by carbonating a Ca(OH)₂ slurry using gaseous CO₂. This method has been used for industrial product improvement, but the use of nanocalcite as a model research system with high purity and surface area has not been explored.

Surface- and bulk-sensitive techniques, including X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), and X-ray diffraction (XRD), indicate negligible contamination from unreacted hydroxyl or trace metals. Further, there was no evidence of other CaCO₃ polymorphs, vaterite or aragonite. SEM showed agglomerations of nanostructured particles and the BET method quantified specific surface area in the range from 13-16 m²/g. IR spectra of industrial calcite, geological calcite (chalk) and nanocalcite displayed distinctly different peak widths, in the order of nanocalcite < chalk < industrial calcite. This indicates that nanocalcite has a relatively high degree of crystallinity and few defects.

This study shows that nanocalcite might improve research results in studies that seek to understand processes in ultrafine geological calcite. Ongoing work will use nanocalcite to more effectively analyze recrystallization rates and surface reaction/adsorption phenomena that are important to aquifer and oil reservoir applications.

**Timing of early solar system homogenization from p-process ¹⁸⁰W heterogeneities**

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**Introduction**

Collapse and subsequent formation of the solar system may have been triggered by a nearby supernova. This can explain the injection of freshly synthesized short-lived radionuclides into the young solar system and can also account for the presence of nucleosynthetic isotope anomalies in meteorites. In order to trace the mixing history of nuclides in the early solar system, we performed the first analyses of one of the rarest isotopes in the solar system, p-process ¹⁸⁰W (ca. 0.1 % relative abundance).

**Methods and Results**

Measurements were conducted using a Neptune ICP-MS, equipped with high sensitivity 10¹² Ohm resistors. For most analyzed iron meteorites, clearly resolvable ¹⁸⁰W excesses (up to +7 ¹⁸⁰W-units) were measured, whereas metals from chondrites and IAB iron meteorites overlap with the terrestrial value. There are distinct ¹⁸⁰W abundance variations between different groups of iron meteorites.

**Discussion and Conclusion**

Our first data provide clear evidence for an increasing homogenization of the early solar system by decreasing ¹⁸⁰W anomalies with decreasing age, suggesting mixing-timescales in the order of several million years. As most asteroidal parent bodies accreted and differentiated during this time span parent nuclides of short lived decay systems may not have been homogeneously distributed in the early solar system.

Because the production of ¹⁸⁰W requires distinct stellar environments, multiple supernovae explosions may have affected the early solar system, thus further weakening the astrophysical view that protostars have formed in relative isolation from their molecular cloud neighbours [1].

Could bacterial residues be an important source of SOM? – A case study from a glacier forefield

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Recently, stocks of soil organic matter (SOM) have been shown to decrease in European soils and also worldwide, which compromises soil fertility and enhances emissions of carbon dioxide to the atmosphere. However, the general structure of SOM, and thereby the mechanisms behind its genesis and loss, remain unclear.

In this framework, microbial biomass is generally regarded to be of low importance for SOM formation. In particular on freshly exposed surfaces, however, bacteria colonize barren mineral surfaces faster than fungi or higher plants. Moreover, recent results indicate that bacterial cell wall fragments frequently occur on soil mineral surfaces and also accompany the microbial colonization of previously clean and sterile activated carbon surfaces after incubation in groundwater. Hence, we hypothesized that, at least, in the initial stages of soil formation bacteria and their fragments may play an important role in particulate SOM formation bearing in mind that most dead organic matter entering the soil is processed by bacteria.

This hypothesis was proven by tracing the development of SOM in a chronosequence with samples from the forefield of a receding glacier (Damma-glacier, Canton Uri, Switzerland) by scanning electron microscopy and other methods. The initially barren mineral surfaces have been shown to be rapidly covered with microbial residues as soil age increases. Moreover, this data compares well to growing C/N-ratios, water contact angles and fatty acid contents in earlier deglaciated samples.

Iron isotope fractionation in soil solutions of a Gleysol

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Analyses of Fe isotope compositions in a Gleysol with petrogleicyc properties from NW Germany yielded bulk δ57Fe values of +0.29‰ (Ah horizon, Fe total ca. 50 g/kg) to −0.30‰ (Bg horizon, Fe total ca. 320 g/kg). A special feature of this Gleysol is a local massive enrichment of Fe (hydr)oxides (comprising mostly goethite and ferrihydrite). In contrast to the overlying CrBg and Bg horizons, the 2Cr horizon which developed from glaciofluvial sands, is characterized by a relatively high δ57Fe value of 40.22‰, but lowest total Fe amounts (ca. 7 g/kg).

To evaluate the relationship of Fe isotope composition of the four horizons and their soil solution, we sampled the soil solution at different depths during spring and autumn. Water of a nearby stream and Fe-rich precipitates in the stream sediments were additionally sampled.

The Fe isotope composition and Fe concentration of the soil solution strongly varied with both depth and abundance of Fe (hydr)oxides, but revealed little seasonal effects. We observed extremely low δ57Fe values of −2.8‰ and Fe concentrations of ca. 3 mg/L in the soil solution of the CrBg horizon. In contrast, the soil solution obtained from the underlying sandy 2Cr horizon is characterized by higher δ57Fe values of −1.5‰ and high Fe concentrations of up to 60 mg/L. The water of the adjacent stream showed δ57Fe values of −0.03‰, whereas the Fe-rich precipitates in the stream bed are marked by a high δ57Fe value of 40.55‰.

We conclude that the low δ57Fe values in the soil solution are the result of preferential adsorption and precipitation of heavy Fe isotopes on abundant Fe (hydr)oxide phases in the CrBg horizon. The Fe-poor 2Cr horizon lacks this capability, therefore, higher δ57Fe values and Fe concentrations are observed in its soil solution. For the Fe-rich precipitates of the stream, preferred removal of heavy Fe isotopes during precipitation entailed high δ57Fe values.
Evaluation of lake biomarkers as indicator of environmental changes along a climatic gradient in Cameroon

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Small crater lakes that have not been exposed to anthropogenic impacts are considered as sensitive recorders of environmental conditions. Here, we studied changes in lipid composition of sediments and water particles organic matter (POM) from lakes, and soils from lake catchments collected in Cameroon along a large environmental gradient (rainfall of ~4000 to 700 mm per year) to evaluate sedimentary lipids as indicators of local and regional environmental changes in the tropics.

Large abundances of an unresolved complex mixture and bacterial lipids in water POM, higher relative concentration of terrestrial refractory lipids in deeper water POM as well as differences in compound distributions and abundances between sedimentary and aquatic lipids indicate intense degradation of primary autochthonous organic matter throughout the water column. No characteristic changes in the distribution patterns of the major compounds, short- and long-chain n-alkanes, n-alkenes, alcohols and fatty acids, in the studied samples along the environmental gradient indicate that distribution of these source-specific biomarkers may not be appropriate to reconstruct ecosystem changes in tropical fossil records. In sediments, tetra- and penta-cyclic triterpenoids, principally consisting of brassicasterol and mainly terrestrial plants-derived stigmasterol and β-sitosterol, increase in abundance with rainfall. Campesterol is identified only in the drier zones. C32-C34 botryococcenes usually associated with the freshwater B. braunii algae were found in soils and lake sediments of the rainiest site. A possible terrestrial contribution of these compounds to lake sediments in this environment will be discussed.

PM$_{2.5}$ chemical composition at rural background site in Central Europe

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PM$_{2.5}$ mass and its chemical composition was studied from Feb 2009 to Mar 2010 at Czech rural backgroud site Košetice. The site is located about 80 km SE from Prague and it is part of EMEP, EUSAAR, and ACTRIS networks. Samples were taken 24 hours each 6th day, in total, 70 samples were analyzed. Besides gravimetry, water soluble ions (IC), elements (PIXE), OC/EC (TOT method) and levoglucosan (GC-MS) were analyzed.

The mass closure was calculated between PM$_{2.5}$ mass and analyzed species. The concentration of crustal elements (Al, Si, Ca, Ti, Fe, Mn were recalculated to their oxides, OC (corrected for positive sampling artifact) and EC were converted to OM resp. EC mass using factor 1.6 resp. 1.1. Using these factors the total analyzed mass was equal to 90% of PM$_{2.5}$ mass determined using gravimetry in average. A resulting average chemical composition of PM$_{2.5}$ mass at Košetice site is shown in the Fig. 1.

![Figure 1: Average composition of PM2.5 at Košetice](image-url)

PM$_{2.5}$ was dominated by OM and secondary inorganic ions. We thank for support to GA CR by grant No.205/09/2055.
That major fault zones strongly influence fluid circulation in detachment faults. In addition, the results of our study suggest both carbon and sulfur from seawater. These hydrothermal systems and control the incorporation of complexes and to moderate temperature, peridotite-hosted on continents show strong similarities to oceanic core oceanic setting near a mid-ocean ridge associated with a strong relation of the Northern Apennine ophiolite to an the Iberian Margin. Field and mineralogical observations show microbial activity, similar to signatures in serpentinites from fluid-rock interaction, but show a strong influence from redox-conditions and microbial activity and their time-integrated changes.

The Northern Apennine ophiolites include serpentinites and ophicalcites that are bounded by shear zones that form domal structures and are characterized by distinct talc-amphibole-chlorite alteration assemblages, which strongly resembles the damage zones associated with detachment faults along ocean ridges. The serpentinites and ophicalcites record multiple phases of seawater infiltration, with initiation of serpentinitization above ~300°C and calcite precipitation at temperatures < ~150°C. The sulfide mineralogy is dominated by pentlandite, pyrrhotite, pyrite, millerite and siegenite, which reflects fairly oxidizing conditions and corresponds to redox-gradients typically found in oceanic serpentinites. The sulfur isotope signatures also indicate a multiphase history of fluid-rock interaction, but show a strong influence from microbial activity, similar to signatures in serpentinites from the Iberian Margin. Field and mineralogical observations show a strong relation of the Northern Apennine ophiolite to an oceanic setting near a mid-ocean ridge associated with detachment faults. In addition, the results of our study suggest that major fault zones strongly influence fluid circulation in these hydrothermal systems and control the incorporation of both carbon and sulfur from seawater.

The Ligurian ophiolite: An analogue to marine serpentinite-hosted hydrothermal systems

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Carbonate-veined mantle sequences in ophiolites exposed on continents show strong similarities to oceanic core complexes and to moderate temperature, peridotite-hosted hydrothermal systems found along slow-spreading ridges. Serpentinitization processes associated with exposure of mantle rocks at the ocean floor thereby play a fundamental role in the global marine bio-geochemical cycles and in mass transfer between seawater and the oceanic lithosphere. Here we present a mineralogical and C and S geochemical study of serpentinites and ophicalcites from an ophiolitic sequence in the Northern Apennine (Italy) and compare this sequence to calcite-veined serpentinites from the Iberian Margin and serpentinites from the basement of the Lost City Hydrothermal Field. The comparison between ancient and modern peridotite-hosted hydrothermal systems provides constraints on fluid pathways, fluid fluxes, redox conditions and microbial activity and their time-integrated changes.

The Northern Apennine ophiolites include serpentinites and ophicalcites that are bounded by shear zones that form domal structures and are characterized by distinct talc-amphibole-chlorite alteration assemblages, which strongly resembles the damage zones associated with detachment faults along ocean ridges. The serpentinites and ophicalcites record multiple phases of seawater infiltration, with initiation of serpentinitization above ~300°C and calcite precipitation at temperatures < ~150°C. The sulfide mineralogy is dominated by pentlandite, pyrrhotite, pyrite, millerite and siegenite, which reflects fairly oxidizing conditions and corresponds to redox-gradients typically found in oceanic serpentinites. The sulfur isotope signatures also indicate a multiphase history of fluid-rock interaction, but show a strong influence from microbial activity, similar to signatures in serpentinites from the Iberian Margin. Field and mineralogical observations show a strong relation of the Northern Apennine ophiolite to an oceanic setting near a mid-ocean ridge associated with detachment faults. In addition, the results of our study suggest that major fault zones strongly influence fluid circulation in these hydrothermal systems and control the incorporation of both carbon and sulfur from seawater.

Base metal ore deposits and marine mineral resources: Rare metal sources for sustainable energies?

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The progress in modern electronic technologies and the need for the use of renewable energies both increase the worldwide demand for metals and metalloids that are critical in high-technology products. There is significant and increasing demand for trace elements like indium, gallium, tellurium, selenium, molybdenum, cadmium, but also for major commodities like nickel, cobalt, copper. The group of so-called ‘electronic metals’ is already an integral part in most technical houseware and office products i.e., computers, notebooks, televisions, cell phones. New technologies and the need for renewable energy concepts in times of global climate changes lead to growing markets in photovoltaic industries. All major worldwide economies face a 20% - target of energy production from renewable energies until 2020. High-efficiency thin-film devices base on metals like indium, gallium, cadmium, tellurium, selenium, molybdenum; their substitution by keeping the high efficiency remains undeveloped. The market situation for these trace elements is tight and demand increases by an increasing number of industrial consumers. Production comes from known ore deposits on land and requires suitable and qualified technical facilities for the recovery of these trace components as by-products from conventional base metal concentrates. Few land-based ore deposits are known to host and produce these trace metals. Production increase, however, is limited due to restrictions on the production of the main commodities, metallurgical constraints, and limited refining capacities. A number of additional ore deposits, however, are capable to meet the demand if more scientific and technical effort is laid on the by-products. As a potential future source, marine mineral resources like manganese nodules, manganese crusts, and polymetallic massive sulfides are locally highly enriched in these trace metals and may define additional reserves. Enrichment factors, elevated concentrations, the mineralogical control, and ore characteristics in base metal deposits represent favourable conditions for the recovery of these metals. The actual production and demand situation is presented for the most important ‘electronic metals’ and the enhanced potential of ore deposits and marine resources in the future supply is discussed.

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Revisiting the age of the Merensky Reef, Bushveld Complex

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The giant Paleoproterozoic Bushveld Complex in the Kaapvaal craton of South Africa may have been emplaced and crystallized in a relatively short period of time [1], perhaps as little as a few million years, followed by rapid cooling [2]. Determination of the absolute duration of Bushveld-related magmatism requires careful application of the single-grain chemical abrasion ID-TIMS, or CA-TIMS, U-Pb zircon method. We recently reported a CA-TIMS zircon age for a sample of the PGE-rich Merensky Reef (West Mine, Rustenburg Section) in the Western Limb of the Bushveld Complex with a weighted mean 207Pb/206Pb age of 2054.4 ± 1.3 Ma (2σ, decay constant errors not included, n = 6) [3]. Use of the EARTHTIME 206Pb-233U-235U tracer and synthetic U/Pb standard solutions now allow for assessing intra- and inter-laboratory reproducibility. We provide a new U-Pb age for zircon from a sample of the Merensky Reef in the Eastern Limb of the complex (Farm Driekop), 2055.30 ± 0.61 Ma (MSWD = 0.43, n = 10), and a revised age based on new analyses for our sample of the reef from the Western Limb, 2056.13 ± 0.70 Ma (MSWD = 0.44, n = 8). All ages were Th-corrected using Th/U = 3, characteristic of the B-1 and B-2 marginal rocks related to the Upper Critical Zone [4]. Compiled results for analyses of the 2000 Ma EarthTime standard solution are 1999.75 ± 0.47 Ma (MSWD = 0.42, n = 18). Analyses conducted at Wyoming by CA-TIMS, with EARTHTIME tracer and standard solutions, on zircon from the Western Limb sample yield a preliminary age of 2056.1 ± 1.1 Ma (MSWD = 0.096, n = 6). This interlaboratory comparison reveals that the crystallization age of the Rustenburg Merensky Reef sample is slightly older than the age reported in [3], although within analytical uncertainty. These results demonstrate the contemporaneity of these Merensky Reef samples, separated by ~300 km, and the potential for distinguishing magmatic events within the Bushveld Complex different in age by 1-2 million years.


Tracking Archean seawater trace metal inventories through multi-proxy analysis of euxinic black shales

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Seawater concentrations of biologically significant and redox-sensitive trace metals have varied through time, reflecting intimate coupling of geological and biological processes in the Earth System. Euxinic black shales, organic carbon-rich mud rocks deposited beneath sulfidic bottom waters, are commonly enriched in such trace metals. Recent work focusing on Mo enrichments have demonstrated the potential to use geochemical analyses of euxinic black shales to track temporal trends in the concentrations of other trace metals in seawater [1].

Multiple episodes of euxinic deposition have recently been identified in the Archean [2–4]. In this study we compare the enrichments of a suite of biologically relevant trace metals (Fe, Mo, Cu and Zn) from Archean euxinic black shales in order to identify temporal trends in their relative abundance in seawater. To strengthen our arguments for faithful preservation of seawater chemistry and to facilitate comparison between Archean shales, as well as comparisons to euxinic shales deposited throughout Earth history, we present our study in the context of additional redox proxies, including TOC, Fe speciation, multiple S isotope analyses and Re-Os systematics.

Seasonal variations in microbial carbon cycling in freshwater wetland sediments identified through rate assays, lipid biomarkers, and porewater geochemistry

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Freshwater wetlands account for about 25% of the annual methane emissions to the atmosphere. A potential positive feedback exists between global warming and the production of this powerful greenhouse gas in sediments. This study explored seasonal variations in the dominant pathways (e.g. methanogenesis) of terminal metabolism in coastal, freshwater wetland sediments from three distinct biogeographic provinces. Through geochemical profiles, microbial rate assays, and lipid biomarker analyses, we assessed seasonal variability in the biogeochemical functioning in coastal Florida, Georgia, and Maine. We evaluated the role of temperature and other seasonal factors on rates and pathways of methane production and consumption, as well as sulphate reduction, acetogenesis, and acetate oxidation, through radiotracer rate assays. Intact polar membrane lipid analyses revealed distinct microbial communities at the three sites which varied with season and depth. The combination of microbial activities, sediment porewater geochemistry, and lipid biomarker analysis provides insight into seasonal fluctuations in microbial-mediated carbon mineralization in freshwater sediments.

Tracing sedimentary pyrite oxidation during managed aquifer recharge

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Oxidation of sedimentary pyrite is often one of the main drivers affecting groundwater quality during managed aquifer recharge [1, 2]. In cases where this leads to the depletion of the sedimentary buffering capacity, groundwater acidification and particularly the associated mobilisation of heavy metals and metalloids (e.g. arsenic) can significantly deteriorate groundwater quality [3, 4]. Data and techniques that allow for a detailed identification and quantification of the mineral reactions are therefore crucial to assess and predict such adverse water quality changes.

The present study examines the feasibility of using stable sulphur isotope analysis as a supporting tool for tracking and characterising pyrite oxidation processes during an aquifer storage and recovery experiment in Perth, Western Australia. During the experiment pyrite oxidation was triggered by the injection of potable aerobic water into a well characterised heterogeneous, anaerobic aquifer. Stable sulphur isotope signals ($\delta^{34}S$) were analysed for sedimentary sulphur species and for aqueous sulphate concentrations in both the ground- and the injectant water in addition to extensive hydrochemical monitoring.

The collected data, including the $\delta^{34}S$ value was interpreted by geochemical and reactive transport modelling. The models were specifically adapted to incorporate all reactions and isotope fractionation processes that affect the evolution of $\delta^{34}S$ in the groundwater and the sediments.

The observed $\delta^{34}S$ data from the monitoring wells indicate that the released sulphate is characterised by a successively changing $\delta^{34}S$ signal during the injection phase. These observed $\delta^{34}S$ trends are thought to result from a highly variable $\delta^{34}S$ composition of the pyrite, which was most likely caused by isotopic fractionation associated with the sulphate reduction that occurred during and/or after the deposition of the sediments.

Mineralogy, geochemistry and age of greisen mineralization in the Li-Rb-Cs-Sn-W deposit Zinnwald, Erzgebirge, Germany

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The Erzgebirge (Krušně hory) is a world class area for Li-Rb-Cs-Sn-W greisen mineralization, which is associated to late-Variscan, postcollisional ‘small intrusion’ Li-F granites in space and time [1]. A typical example is the Zinnwald/Cínovec Li-Rb-Cs-Sn-W deposit, which is hosted by the Cínovec-Zinnwald granite cupola and Teplice rhyolite. Sn-W-Li mining was active for about 700 years until 1990. The exposed intrusion (1.3 x 0.3 km) is composed of a Li-F-granite which in part is strongly greisenized by high-temperature fluids [1, 2]. The flat dipping quartz-zinnwaldite-topaz-fluorite cassiterite greisen ore bodies in the German part of the Zinnwald deposit have a thickness of up to 25 m and resources of about 50 kt Li, 19.5 kt Rb, 1 kt Cs, 6.7 kt Sn, and 2.7 kt W [3]. Three representative zinnwaldite-rich quartz-Li-mica-topaz-cassiterite greisen samples with a total weight of 30 t were taken in two levels of the old mining area. The average bulk geochemistry and the range of 16 greisen subsamples indicate the high concentrations of rare elements and fluorine: Li (3290, 490-6990 ppm); Rb (2320, 440-4900 ppm); Cs (67, 13-160 ppm); Sn (1620, 52-153 ppm); F (2.7, 0.36-4.3 wt.%); Th (38, 22-85 ppm). The geochemical signature (e.g., relatively high Li, Rb, Cs, F, Nb, Sn) of the greisen and Li-F granite show similar trends [1, 3]. Seven Li-mica separates have been dated by Ar-Ar in Freiberg (ALF) using laser step heating techniques and an ARGUS multicollector noble gas mass spectrometer. Ages are interpreted as near-formation ages of Li-mica and range between 312.6 ± 2.1 Ma and 314.9 ± 2.3 Ma (2o external).


Analysis of iodine, bromine and chlorine in marine sediments and carbonate nodules by ICP-MS

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Halogenes are thought to be useful in the geochemical studies of rock and sediment formation. However, their analyses are difficult due to their low abundances, specifically Br and I. There are lack of reliable analytical results also for standard rocks. Therefore, we have examined separation procedures of Cl, Br and I from sediments and sedimentary rock samples by pyrohydrolysis. Halogens evaporated by pyrohydrolysis collected in trap solutions. The concentrations of Br and I were determined by ICP-MS and that of Cl was measured by ion-chromatography.

Using the developed methods, we have analysed Cl, Br and I in various standard rock samples. The analytical results agreed well with certified values. New data for standard rocks (e.g. JMS-1, JMS-2, JCP-1, JC-1), in which the concentrations were not known, were also obtained.

We also analyzed sediments and carbonate nodules collected from methane hydrate areas in Japan Sea. In these areas, high iodine concentrations were observed in pore waters in the sediments. We also analysed Br and Cl for comparison. Results obtained for these elements in solid phase of the sediments were in the ranges: Cl: 5000-10000 ppm, Br: 40-150 ppm, I: 10-200 ppm. High iodine concentrations are characterized by methane hydrate areas. Concentrations of Br and I showed the decreasing tendency with depth. Markedly high values of I in surface sediment was observed. This suggested that I was accumulated by the deposition of organic matters from seawater and also by the fixation in oxic layer of the sediments from pore water. The concentrations of Cl, Br and I in carbonate nodules were about 100 ppm, 7 ppm, 4.6 ppm. I in carbonate nodules was found to be highly concentrated from pore water compared with Br. The I/Br ratios in carbonate nodules were much higher than those in pore water and solid phase of the sediments. Concentration mechanisms of the iodine is being examined now.
Identifying the when and where of oil
generation using platinum,
palladium, osmium and rhenium
geochemistry

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Understanding the timing and source of petroleum
generation permits more successful oil exploration and
recovery. Traditionally, oil source rock identification uses
organic chemical analysis of light oil fractions. However,
common processes such as biodegradation preferentially
removes light hydrocarbons from petroleum compromising
traditional oil to source fingerprinting techniques. We
therefore developed a new geochemical technique, which not
only absolutely dates oil generation through Re–Os
geochronology, but also enables the identification of source
units through the comparison of 187Os/188Os at the
time of generation (Osg) and Platinum/Palladium (Pt/Pd) ratios
in oils and their potential source units. We demonstrate the
applicability of this method in the well understood United
Kingdom Atlantic Margin (UKAM) petroleum system and
then apply it to identify the source of the West Canadian Tar
Sands (WCTS).

Our data yields a Re–Os age of 68±13 Ma (MSWD=20)
for oils of the UKAM, indistinguishable from published basin
models. Furthermore, the Os
g and Pt/Pd values of these oils are
indistinguishable from those of the known source rock,
demonstrating that Os
g and Pt/Pd values can be used to
distinguish oil source. When applied to the WCTS, comparison
of Pt/Pd and Os
g values with the three potential source units
suggests that the dominant source unit is the late Jurassic
Gordonale Fm. with only minor inputs from other sources
(e.g. Devonian-Mississippian Exshaw Formation).

Unlike traditional organic geochemistry, Pt/Pd and Os
g fingerprinting is not rendered ineffective by biodegradation
allowing oil source correlation in previously unsuitable
petroleum systems and the deduction of migration pathways.
Combining Re–Os geochronology with Pt and Pd
geochemistry has identified the Gordonale Fm. as the source
of the WCTS. This now permits both spatial and temporal
constraints on petroleum systems to be established and
therefore provide a significant tool for petroleum system
exploration and development.

Bio-Au nanoparticles on archaelaeal and
bacterial S-layers

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Gold nanoparticles with substantially different properties
were produced by using two alternative S-layer templates. The
first one was a bacterial template, representing sheets of the S-
layer of Bacillus sphaericus; the second one was in a form of
empty cells (ghosts) consisting of the so-called SlaA-layer of
the thermoacidophilic archaean Sulfolobus acidocaldarius.
The archaelaeal SlaA-layer is resistant not only to high
temperatures and acidity but also to detergents, that allowed to
purify the SlaA-layer-ghosts keeping the shape of the cells.
The production of the Au nanoparticles was performed
according to [1, 2] in a two-step procedure by using DMAB as
a reducing agent.

We demonstrate that the SlaA-ghosts of S. acidocaldarius
serve as a very efficient template for complete reduction of
Au(III) to Au(0). In the case of using S-layer sheets of B.
sphaericus only 40 % of the added Au(III) was reduced to Au
(0) [2]. The size of the archaelaeal bio-Au nanoparticles was
about 2.5 nm, while those of the bacterial ones was about 4
nm. The most striking property of the archaelaeal bio-Au
nanoparticles is, however, that they are paramagnetic, in
contrast to the bacterial ones and also to bulk gold, which are
diamagnetic. As demonstrated by SQUID magnetometry, the
archaelaeal bio-Au possesses an unusually large magnetic
moment of about 0.1 µ B/Au atom. HR-TEM combined with
EDX analysis revealed that the archaeal Au nanoparticles are
bound to sulfur atoms. The latter originate from the thiol
groups of the cystein amino acid residues which are
characteristic for the SlaA-layer of S. acidocaldarius but
absent in the S-layer of B. sphaericus. Surprisingly, the
magnetic moment of the archaelaeal bio-Au nanoparticles
is substantially larger than the ones observed for thiol capped,
chemically produced Au nanoclusters [3]. We suggest that the
unusual shape and the biochemical characteristics of the SlaA-
ghosts are responsible for the observed extraordinary
properties of the archaelaeal bio-Au.

Combined U-Pb zircon dating and apatite trace element compositions applied to Paleozoic tephrochronology

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The global utility of a stratigraphic section that records important Earth history events requires a robust geological timescale. This could be accomplished either by establishing highly precise and accurate ages for the section in question or by accurately correlating strata in the section of interest to those regions where a well-developed time scale has already been established. For pre-Cenozoic rocks the challenge of developing independent age constraints for any given section of rock increases with age.

An anomalously high abundance of tephra in the Late Ordovician of eastern North America and Scandinavia presents a unique opportunity to test aspects of the importance of high-precision U-Pb zircon geochronology combined with the utility of crystal-chemistry based tephrochronology. Specifically, high-precision ages combined with robust crystal chemical data can be assessed in view of its ability to help understand aspects of the Great Ordovician Biodiversification Event, end-Ordovician mass extinctions, various oceanic carbon isotope events, and the end-Ordovician glaciation. A few of the widespread tephra possibly derive from the largest known eruptions in the Phanerozoic, which may have triggered important biotic and climatic responses. Tephrostratigraphic correlation of these large eruptive units has been challenging beyond several 100’s of square kilometers because the tephra are heavily altered and span different depositional and tectonic settings. Volcanogenic apatite trace element concentrations (Mg, Cl, Mn, Fe, Y, and Ce) have been successfully applied to these tephra correlation problems in the eastern U.S. and between North America and Europe. This apatite trace element tephrochronologic approach has been invaluable for investigating several chronostratigraphic schemes related to Ordovician biostratigraphy, chemostratigraphy, and sequence stratigraphy. Our new U-Pb zircon and apatite trace element data shows that there is some significant disparity in previously assumed temporal relationships, particularly between widely spaced locations.

Exoplanet atmospheres: From hot to habitable worlds

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Current observational techniques allow us to detect a broad variety of extrasolar planets. In some cases we can measure properties such as the planetary radius, mass and temperature and constrain the structure, molecular composition and dynamics of their atmospheres. The diversity of observed exoplanets is extraordinary in terms of planetary system architectures, physical conditions and chemical compositions. I will present several striking cases that illustrate this diversity.

At two extremes of the known sample of exoplanets are hot gas giants, whose atmospheres constitute a puzzle for both physicists and chemists, and potentially "habitable" worlds which, despite very exotic properties, could host liquid water. I will focus on these two types of atmospheres and show that their modeling is a challenging but extremely rich subject. I will then discuss the prospects for the next step of exoplanet characterization.
A chlorine isotope view of mantle metasomatism via slab fluids/melts

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We use Cl, H and O stable isotope geochemistry to investigate fluid/melt infiltration of the Finero peridotite (Ivrea Zone) in a shallow mantle wedge setting (1.2-1.6 GPa, ~900°C, Perple_X modelling). Unaltered samples from the Balmuccia peridotite have typical mantle $\delta^{37}$Cl values of -0.4±0.3‰ and provide a reference frame for the metasomatized rocks. Four lithologies from Finero (1: spinel harzburgites with minor amphibolite, 2: harzburgites with abundant phlogopite, 3: amphibolite segregations, and 4: phlogopite segregations) have $\delta^{37}$Cl values between -2.0 and +2.1‰ (Fig. 1). We also report preliminary chlorine isotope data from HP/UHP rocks (hydrothermally altered oceanic crust, serpentinites with rodingite dikes, and Mn-rich and calcic schists) that represent likely subduction inputs (Fig. 1). The isotopic variability recorded at Finero cannot be reconciled with metasomatism by a single fluid. Three principal components describe the sample variability: (A) endmember peridotite, (B) a low $\delta^{37}$Cl, high $\delta^{18}$O component (melt derived from subducted sediment), and (C) a high $\delta^{37}$Cl, $\delta^{18}$O, $\delta^{13}$C, and [Cl], [K] component (high-salinity fluid likely released from altered oceanic crust). Preserved cm-scale isotopic heterogeneities indicate channelized infiltration of fluid/melt at different times and from different slab source rocks. Small-scale fluid release events – not just large-scale serpentinization dehydration – are thus important in chemical transfer from subducted slabs to the mantle wedge.

Figure 1: Box-and-whisker plot of $\delta^{37}$Cl values from unaltered mantle peridotite (BAL), metasomatized Finero rocks, and various HP and UHP rocks from the western Alps.

Correlation of $\delta^{13}$C and PGE contents in magmatic ores

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Typically, the spatial association of rare metals, including PGE, with the organic matter is regarded as an argument to the important role of organic matter in ore formation. As an example, ore deposit in black shales is given [1]. However, there are also many sedimentary basins with low metal concentrations. Thus, ore mineralization occurrences in black shales are not a reliable criterion for genetic connection: mineralization – organic matter. Mineralized geological formations with low contents of reduced carbon are best suited to reveal such relations.

The example of correlation between the isotopic composition of carbon, its content and PGE concentrations in the ores of one of the deposits of the northwestern Siberian platform is presented in this study. Carbon isotope composition were determined using Thermo Finnigan 253 mass spectrometer with specially-constructed line [2]. Special attention was paid for the signal from neutral C0 species (graphite, solid solution C) in the isotopic analysis. The contents of this carbon in the samples range from 15 to 80 ppm. $\delta^{13}$C values were mainly in the range of -21 to -26, 5‰. In rare cases, heavier isotope values were obtained for graphite: -12; -13, 5; -14, 5‰. Data have shown that there is no correlation between carbon contents and PGE concentrations (correlation coefficient is 0.45). However, the comparison of PGE contents in ores and carbon isotope values (C0) has shown the complete linear dependence (the correlation coefficient is 0.94) between them: the weighting of carbon isotope composition was accompanied by the increasing of PGE contents in the same samples. Such a weighting of carbon isotope composition was noted earlier by Ryabov et al. [3]. The most possible explanations of the results is that platinum group elements are transfered by specific organometallic compounds rather than the whole organic matter.

Petrogenesis of mantle peridotites from the Kizildag ophiolite (SE Turkey): Implications from mineral composition

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Kizildag (Hatay, SE Turkey) ophiolitic complex is one of the best maintained Tethyan lithospheric remnants of Turkey ophiolites. Mantle tectonites from the Kizildag ophiolite contains spinel with Cr# 0.47-0.61 which indicates that they are residue of ~23-30% of partial melting of primitive upper mantle, and are similar to the supra subduction zone peridotites. Pyroxenes have lower content of Al (Al2O3(Cpx)=1.61-2.77 wt%) and Ti (TiO2(Cpx)<0.25), and also indicate the respectively high degree of depletion. Clinopyroxene from the twelve peridotite samples of Kizildag ophiolite complex analyzed by LA-ICP MS for their trace and REE contents. Clinopyroxenes from mantle tectonites show LREE enrichment (SmN/LuN=0.04-0.78) and nearly horizontal HREE (ErN/LuN=0.49-1.32) patterns. There is a negative correlation between Sm/Yb vs. Yb contents of clinopyroxenes, which consistent with the hydrous partial melting and fluid-melt enrichment trend. There is also a negative correlation between Yb content in clinopyrexene and Cr# of spinel. The depleted composition of incompatible elements and LREE enriched pattern known as an evidence for mantle-melt interaction. There is a good correlation between Cr# of spinel and HREE concentration of clinopyroxenes. However, chondrite-normalized Ce concentrations (Ce)N of clinopyroxene in mantle tectonites of Kizildag ophiolite is higher (0.10-0.13ppm) than the abyssal peridotites. The mineral chemistry results indicate that the mantle tectonites shows higher degree of partial melting than abyssal peridotites. Subducting oceanic lithosphere produces LREE-enriched melt and/or fluids and this is resulted with the higher melting. These evidences indicate an arc magmatism i.e. a suprasubduction zone setting fort he genesis of Kizildag ophiolite.

Human impact on global element cycles

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Material flow caused by human actions has become a major component of the Earth’s biogeochemical cycles. In order to constrain the effect of human activity on global elemental cycles, Klee and Graedel [1] quantified the magnitude of anthropogenic activities on 77 of the naturally occurring elements. Their study compiled estimates of natural (weathering of continental crust, net primary production, element mobilized through sea spray) and anthropogenic (mining, biomass burning, and fossil fuel combustion) element fluxes and determined the role of humans on global elemental cycles. While Klee and Graedel [1] assessed the role of a number of important natural and anthropogenic processes, their assessment was not comprehensive. For instance, global dust fluxes [2] and losses to and gains from the extraterrestrial environment were not considered.

Here we revisit the Klee and Graedel [1] study and add important sources (chemical flux contributions from volcanoes and aeolian dust, input of extraterrestrial matter) that affect global elemental cycles. In addition, we updated chemical inventories and fluxes for a range of processes.

Our calculation shows a substantial change from the original Klee and Graedel [1] study. Geochemical cycle of 22 elements are dominated by human actions. Biogeochemical cycle of gold, platinum, palladium, rhenium and iridium are dominated by anthropogenic activities, followed by chromium, antimony, copper, mercury, rhodium, lead, bismuth, tin, tellurium, cesium, arsenic, tungsten, iron, silver, nickel, indium and uranium.

Assessments of the anthropogenic radiative forcing over the Amazon Basin: Aerosols and land-use change

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Man-made biomass burning activities that occur yearly in the Amazon send large amounts of smoke to the atmosphere, and alter the landscape by converting forested areas into pastures and cropland. This work addresses the radiative forcing (RF) of the smoke aerosol and of the land cover change in Amazonia, seeking to quantify their climatic impact over the Earth System.

The cloud-free direct RF due to biomass burning aerosols was derived from the CERES sensor (Clouds and the Earth’s Radiant Energy System) [1] flux retrievals over the Amazon from 2000 to 2009, considering the peak of the burning season from August to September. The Amazon Basin was divided in 0.5° latitude-longitude grid cells according to [2], and the broadband shortwave (0.3 to 5.0 µm) radiation flux was regressed against the aerosol optical depth to determine the radiative flux under clean (no aerosol) conditions, \( F_{cl} \). The direct RF was derived by subtracting from \( F_{cl} \) the flux under average aerosol conditions. The resulting aerosol RF shows large spatial and temporal variations, with an average of \(-57 \text{ W/m}^2\) at 440 nm, large spatial and temporal variations, with an average of \(-56.0°\)E for the 2007 burning season the cloud-free spectral direct aerosol RF was estimated as \(-57 \text{ W/m}^2\) at 440 nm, \(-17 \text{ W/m}^2\) at 675 nm, \(+11 \text{ W/m}^2\) at 870 nm, and \(+6 \text{ W/m}^2\) at 1020 nm.

The RF due to land-use (albedo) change was estimated for clean (no aerosol) conditions over the state of Rondonia, Brazil, an area that has been heavily deforested since the 70’s. Surface reflectance retrievals from MODIS (Moderate Resolution Imaging Spectroradiometer) were used to select study areas, and the RF was computed as the difference between the CERES radiative flux at the top of the atmosphere above forests and over nearly bare-ground deforested patches.

The albedo land-use change RF was \(-56.0°\)E for the 2007 burning season the cloud-free spectral direct aerosol RF was estimated as \(-57 \text{ W/m}^2\) at 440 nm, \(-17 \text{ W/m}^2\) at 675 nm, \(+11 \text{ W/m}^2\) at 870 nm, and \(+6 \text{ W/m}^2\) at 1020 nm.

The albedo land-use change RF was estimated as \(-22±3 \text{ W/m}^2\), a figure that can be compared to the direct aerosol RF, but in the Amazon these deforestation patches correspond to a nearly permanent modification of the surface albedo that also changes the local radiation budget.

Studies of the indirect (i.e. mediated by clouds) aerosol forcing over the Amazon Basin are currently under way and they will help throwing in one more puzzle piece to the set above, depicting key factors that define the human RF over the Amazon.


Osmium isotope signatures in peridotites from the ultra-slow spreading SWIR and RTJ

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The ridge magmatic systems are the places where crust directly forms. They provide information on how different crust forms depending on variable spreading rates associated with amount of melt supply and the source of the supplied melts. The central part of the Southwest Indian Ridge (SWIR), known as an ultra-slow spreading system (14-16 mm/yr) was investigated. We had two cruises of R/V Hakuho-Maru in 2008 (KH07-4 Leg2) and 2010 (KH09-5 Leg4) R/V Hakuho-Maru and dredged aphyric to porphyritic basalts, peridotites, metamorphic and sedimentary rocks from 17 sites from 34E to 40E along SWIR. We also sampled peridotites from the Rodriguez Triple Junction (RTJ) where three ridge system, the Central Indian Ridge, the Southeast Indian Ridge and SWIR meet together (YK05-16 Leg1 at 2005 by R/V Yokosuka and Shinkai 6500).

The Re- Os isotope systematics were investigated to identify the source of basalts and peridotites. One of the major advantages using Re-Os system is that they are relatively robust to secondary effects, e.g. sea water alteration and mantle metasomatism. The Os isotope ratios of peridotites from SWIR and from RTJ are \( ^{187}\text{Os}/^{188}\text{Os} = 0.1239-0.1307 \), which are in the range of those reported as abyssal peridotites. The Os isotope ratios of spinels from SWIR, however, indicate more depleted signature; around \( ^{187}\text{Os}/^{188}\text{Os} = 0.121 \), compared to the primitive upper mantle \( ^{187}\text{Os}/^{188}\text{Os} = 0.1296 \), [1] and peridotites from SWIR of this study and [2]. Such mismatches of Os isotope ratios between the spinels and the peridotites have been also reported even within a hand specimen level [2]. The time of Rhenium depletion (\( T_{\text{RD}} \)) ages were estimated as around 1Ga for these spinels, which show that the host peridotites of spinels experienced melt extraction at least around 1Ga even they were recovered from the currently active ridge.

Molybdenite deposition in Bingham Canyon deposit: Role of sulfur, redox and pH chemistry in magmatic-hydrothermal fluids

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The Bingham Canyon porphyry deposit shows a distinct metal zonation of 1) shallow Cu-Au mineralization (Cu-stage) and 2) deeper Mo mineralization (Mo-stage) occurring in a separate vein set that truncates earlier Cu-Au veins.

In deep low-grade Cu-stage quartz veins, we found high concentrations of Cu, S, and Mo in the fluids, whereas in low-grade Mo-stage veins, we found rather lower Cu, but similar concentrations of S and Mo, compared to the input fluids of the Cu-stage. Sulfur concentrations in intermediate density (ID) type inclusion in deep low-grade Cu-stage samples are similar to their Cu concentration, whereas ID-type inclusions in low-grade Mo-stage veins have S contents in excess over their Cu content. Compared to the P-T conditions of the Cu-precipitation stage (90-260 bars and 320-430 °C), the Mo-precipitating fluids extended to higher pressures and temperatures of 140-710 bars and 360-580 °C.

Mass-balance calculation and vapor/brine partitioning data indicate that the mass of vapor phase exceeded that of brine by about 9/1 and more than 70% of Mo, Cu, and S (by mass) were deposited by the vapor phase in both mineralization stages.

High Mo contents (max. 0.0054 Mo/Na in ID; 380 µg/g Mo in brine) in the hydrothermal fluids were maintained from the early Cu-stage to the late Mo-stage, suggesting that Mo concentration in the fluids may not be the decisive factor for the separate Cu & Mo precipitations in Bingham Canyon deposit. Instead, the metal separation may be explained by a reduction in redox and a pH increase in the fluids from evolving source region. This is indicated by 1) the stoichiometry of chalcopyrite and molybdenite precipitation reactions, 2) a difference in the Fe/Mn ratio in fluids of the two (Cu and Mo) veining stages, 3) incipient muscovite alteration along high-temperature molybdenite veins, and 4) an increasing vapor/brine partition for Mo.

We suggest that the early Cu-stage fluids were slightly oxidized, allowing efficient Cu-Fe sulfides precipitation and thereby consume much of the dissolved S. By contrast during the later Mo-stage, the fluids were more reduced and acidic, thereby allowing selective saturation of molybdenite as the first precipitating sulfide.

Uranium interactions with bacterial communities from contaminated soils in Chernobyl

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Following the Chernobyl accident in 1986, vegetation, contaminated soil and other radioactive debris were shortly buried in situ in trenches. The present work describes the analysis of the structure of the bacterial communities that have been evolving in this environment for more than 20 years. Comparison of the diversities found in soil samples exhibiting contrasted radionuclides content is a prerequisite to point out the potential role of microorganisms in radionuclide migration in soils.

Bacterial communities were examined using a genetic fingerprinting method that allowed a comparative profiling of the samples (DGGE), with universal and group-specific PCR primers. Our results indicate that a long term exposure to radionuclides did not lead to extinction of bacterial diversity in Chernobyl soils.

A collection of aerobic and anaerobic cultivable isolates was also assembled. A phylogenetic analysis of 250 heterotrophic aerobic isolates revealed that 5 phyla are represented: Beta-, Gammaproteobacteria, Actinobacteria, Bacteroidetes and spore-forming Firmicutes, the last being largely dominant [1].

Eleven representative fast-growing strains, related to diverse genera, were exposed to uranium. In each case, bacteria/uranium interactions exhibited different kinetics, suggesting that underlying mechanisms (biosorption, accumulation, precipitation) could be different.

Biomineralization of Fe$^{II}$-Fe$^{III}$ green rust in γ-FeOOH coated sand column under saturated flow conditions

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The synthesis of Fe(II)–Fe(III) green rusts (GR) in environmental and engineering systems is a challenging project due to the higher reactivity of GR towards a panel of organic or inorganic pollutants. While the biomineralization and stabilization of GR have been well described in batch reactor from ferric oxide respiration by Shewanella putrefaciens [1, 2] or mixed cultures of bacteria [3, 4], their formation routes as a main secondary iron mineral under flow-through conditions remain undescribed.

Figure 1: Picture of a green rust (GR) crystal obtained in a lepidocrocite (L) sand packed column inoculated with S. putrefaciens and fed with formate as electron donor.

Formation of both GR and magnetite was observed in a lepidocrocite-coated sand packed column at a flow rate of 0.1 mL/min. However, GR was the dominant secondary mineral when silicate was present in the injected feed solution (Fig.1). In this latter case, untransformed lepidocrocite was still present in the sand packed column. This behavior could be explained by the sorption of dissolved silicate on the lepidocrocite surface, which might hinder the reactive sites and so limit the bioreduction extent. On the other hand, the interactions of dissolved Si with the lateral faces of the GR crystals could stabilize the GR structure, thus preventing its transformation into magnetite.

Hg (II) sequestration by ettringite-type phases. A geochemical modeling and EXAFS study

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Sequestration of Hg by ettringite-type phases (Ca$_6$[Al(OH)$_6$]$_2$(SO$_4$)$_3$.26H$_2$O), formed during hydration of Portland-type and super-sulfate cements, as a potential method for sediment remediation was investigated theoretically with a kinetic-equilibrium model and experimentally in co-precipitation (Hg+Al+SO$_4$+Ca and Hg+Fe+SO$_4$+Ca systems) and substrate-amended (quartz, clay, and/or sediment) batch experiments in aqueous NaCl solutions. Geochemical modeling predicted formation of ettringite and calcium-silicate-hydrate (C-S-H) gels as a function of reaction time, corroborating XRD results for amendment batch experiments. XRD patterns of the co-precipitation products showed Al- ettringite and gypsum as the main mineral phases in the Hg+Al+SO$_4$+Ca and Hg+Fe+SO$_4$+Ca systems, respectively. Extraction results indicated that <20% of added Hg was associated with the exchangeable fraction in both co-precipitation and substrate-amended batch experiment. XAS and electron microprobe characterization of the Hg co-precipitation and cement hydration products suggests physical micro-encapsulation of Hg in ettringite as a polynuclear chloromercury calcium precipitate. Hg XAS analysis of the solid products in the Hg+Fe+SO$_4$+Ca system indicated Hg sorption on ferrihydrite as the main retention mechanism. These results revealed that, in the presence of Cl -, Hg immobilization in cement systems is kinetically controlled by Hg-Cl complexation and precipitation of cement hydration products. However, in high Fe systems, Hg retention predominantly as the Hg (OH)$_2$ species, is controlled by fast sorption equilibrium on ferrihydrite.

Experimental study of mineral equilibria in the system Li$_2$O-K$_2$O-Al$_2$O$_3$-SiO$_2$-HF-H$_2$O (with topaz) at 400°C and 100 MPa

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The experimental study of mineral equilibria in the system Li$_2$O-K$_2$O-Al$_2$O$_3$-SiO$_2$-HF-H$_2$O was carried out to determine influence of composition of solution (lithium content) on genesis of greisen deposits.

Topaz one of the major indicators of F-bearing minerals participating in most of the studied reactions. Experiments were performed in autoclaves in gold ampules with self-sealing shutter by a technique of monovariant reaction. This technique is based on change of topaz grain weight. All the mineral phases participating in the reaction were placed together into ampoules. The topaz was used as rounded grain whereas other components of reactions were added as powder.

As a result influence of lithium on shift of topaz stability field on the diagram lg (mHF) - lg (mKF) established earlier [1] for modeling system K$_2$O-Al$_2$O$_3$-SiO$_2$-HF-H$_2$O has been estimated. At low concentration of LiF and high concentration of HF in the solution the line limiting the topaz field for monovariant equilibrium topaz-AlF$_3$ moves downwards to the axis lg (mHF). Muscovite stability field is replaced by lepidolite field at relatively high concentration of LiF and low concentration HF in the solution. Absence of potassium in the solution leads to formation of the lithium-bearing alumina-fluoride phase.


Krypton and xenon in air bubbles from ice cores as tracers of past ocean temperature

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The heavy noble gases krypton and xenon are quite soluble in liquid water, with a strong temperature-dependence of the solubility. Because the total inventory of these gases in the ocean-atmosphere system is constant, an increase in the oceanic inventory must be accompanied by a complementary decrease in the atmospheric inventory. Dinitrogen (N$_2$) gas is much less soluble and so its atmospheric inventory is little affected by ocean temperature change. Sources and sinks of N$_2$ may be neglected due to the great abundance of this gas in the atmosphere, and the fact that the entire denitrifiable inventory of N comprises less than 0.01% of the atmospheric pool. Thus the ratios Kr/N$_2$ and Xe/N$_2$ in the past atmosphere should predominantly reflect past ocean temperature change. These parameters may be estimated from measurements of trapped air composition in ice cores, making appropriate corrections for gravitational settling and thermal fractionation that occurred in the snow layer (firn) at the ice core site.

Measurements are done by classical dual- dynamic-inlet electron impact mass spectrometry on air melt-extracted from 1 kg of ice, and encompass the krypton isotope pair $^{86}$Kr/$^{82}$Kr and $^{15}$N/$^{14}$N for the purpose of making the gravity and thermal corrections.

This new proxy reflects mean ocean temperature change, albeit slightly weighted toward the cold end of the temperature distribution due to the greater solubility of these gases in cold water. Because the ocean’s heat and gas burdens are set at the outcrop where air-sea equilibration last occurs, and they travel through the ocean interior nearly adiabatically and conservatively, there is no time lag between changes in ocean heat content and changes in atmospheric noble gas burden. Consideration of the solubilities and relative volumes of the reservoirs leads to the prediction that a 1°C warming will produce a +0.5‰ increase in atmospheric Kr/N$_2$. Current measurement precision is around 0.2‰ for a 1-kg piece of ice, suggesting a precision of about 0.4°C for this proxy. Recontructions over the past glacial cycle suggest a glacial mean ocean temperature about 3°C colder than present, with a rapid warming of about 2°C between 18-15 ka. This was a time period of rapid atmospheric CO$_2$ increase, consistent with the hypothesis that atmospheric CO$_2$ lowering in the glacial episodes was caused by sequestration in a poorly ventilated, dense, cold deep water layer.
**Enhanced in situ methanogenesis and microbial community analysis of coal beds**

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Biogenic methane has enormous potential as a sustainable energy source and is found in a wide variety of subsurface, anaerobic, hydrocarbon bearing environments. The Powder River Basin in Wyoming, USA is an area previously shown to be an active ‘geobioreactor’, or an area where active in situ methanogenesis occurs as determined by coal conversion to methane in laboratory experiments, the presence of metabolic intermediates in coalbed methane formation waters, and the ability of the consortia present in these waters to convert the metabolites to methane. Understanding the composition and metabolism of the methanogenic consortia has been one of several key steps in commercializing the process of sustainable biogenic methane production.

In order to identify the microbes present in these methanogenic consortia, we performed microbial community analysis using error-correcting barcode pyrosequencing analyzed with the QIIME bioinformatic pipeline. This involved hundreds of samples collected from different locations within a set geographical area over several years. We used both bacterial and archaeal specific primers to amplify these distinct populations from our DNA samples. The QIIME pipeline was used for library demultiplexing, OTU picking, alignment, taxonomic identification, and statistical analysis of community structure using Unifrac. Spotfire was used for visualization of QIIME results with metadata from the formation.

Here we demonstrate the large scale areal and temporal sampling for community analysis of coalbed methane (CBM) wells within a discrete but large area of the Powder River Basin. Temporal consists of the baseline state, followed by a bio-stimulation phase (i.e. Restoration) and enhanced methane production phase. Under baseline conditions, we find distinct bacterial and archaeal populations that vary by coal, water chemistry, and time. Community profile signatures help determine the areas of greatest methanogenic potential and identify patterns of ground water recharge, water movement, and potential metabolic bottlenecks. Data will be presented showing increased gas production over pre-restoration decline curves, the period of enhanced methane production and the observed changes in the microbial community structure associated with enhanced gas generation.

**An Exafs and ab initio study of aquated Cd^{2+} and chlorocadmium(II) complexes up to 300°C**

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The hydrothermal transport and deposition chemistry of cadmium in the Earth’s crust is still poorly known. X-ray absorption spectroscopy and quantum chemical calculations can provide fundamental insight on a molecular level into the formation/stability and hydration of the geochemically relevant Cd(II) complexes.

We have measured the EXAFS of aqueous cadmium nitrate, perchlorate and chloride solutions up to 300°C and at the equilibrium saturated vapour pressure using an X-ray optical cell employing silica glass windows. In dilute nitrate solutions ((0.01m Cd(NO_3)_2/0.01m HNO_3), Cd^{2+} is coordinated to 6 water molecules over the temperature range from 25 to 250°C. There is a small electrostrictive contraction of the Cd-water distance from 2.27 to 2.23Å with increasing temperature as the water solvent properties change at conditions along the two phase curve. In more concentrated nitrate and perchlorate solutions (1.00m), the mono-, di- and trinitato- and monoperchloratocadmium (II) ion pairs were detected. The stepwise formation of chlorocadmium (II) complexes was also studied from 25 to 300°C in solutions having HCl concentrations from 0.001 to 3.00m. For example, in 3.00m HCl, the CdCl_{2}^2 species predominated over the entire temperature range with the Cd-Cl distance remaining essentially constant at 2.46-2.45Å.

The computational part of the study was designed to provide further insight into the nature of Cd^{2+} hydration as well as to the coordination and hydration of the cadmium chloride complexes. We performed a systematic survey of the equilibrium geometries of CdCl_{m} (H_2O)_n for m=0-4 and n=0-11. We employed the cc-pVnZ (PP) (n=D, T) correlation consistent basis set for Cd, cc-pV (d+nn)Z (n=D, T) for Cl and cc-pVnZ (n=D, T) for H and O (abbreviated as VnZ (PP) (n=D, T). Geometry optimisations for the various hydrated complexes were performed at the RHF and the results thereof then applied as starting geometries for subsequent MP2 level calculations. In the case of Cd (H_2O)_6^{2+} for example, the optimal Cd-O distance is 2.28Å. If 7 waters are constrained to the first shell, then the distance extends to 2.35Å, however, this geometry with 7H_2O is unstable.
Composition modeling of pollution of groundwater by usage of geoelectrical and hydrogeochemical studies

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Now a day, the use of indirect methods of measurement and detection of groundwater contamination due to high speed and lower cost is interested. Among the geophysical methods are very important. in this project was trying, with sampling of groundwater resources and their chemical analysis and Select the appropriate method, and the effect of trace pollutants using the results in comparison to groundwater modeling with integrated studies and hydrogeochemical and geoelectrical was acting.

Thirteen profiles with the schlumberger array with south to north in the direction have been picked in study area. General review of the main geoelectrical sections are shown four layers and in some places raise up to six layers. To achieve good picture of the situation in depth, plans are extracted in different depths. These maps are identified manner and distribution of lateral variations of electrical resistance of geological formations.

Figure 1: fence of 3d resistance modeling

10-meter depth Plan trend shows a noticeable decrease in the amount of resistivity is observed, especially in the south, it's the main zone of contamination, probably. These studies with samples from 69 water wells were investigated fully consolidated.

Discussion of Results

Results showed that the electrical resistance of contamination zone is lower than usual about the same sedimentary unit which is caused by the effect of pollutants. Based on field observations in the vicinity of this area there are water channel which converted this area to a washed zone that contaminations can penetrate into the soil with infiltrated water.

Geochemical zoning analysis based on ‘Axes Level’ innovative method

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Primary Geochemical halo and alteration zones around ore deposits with the phenomenon formation of ore deposits in a relationship are genetic. So that the diagnosis clear boundary between alteration regions and geochemical alteration halo not be always possible. Observations have shown that spatial distribution (longitudinal, lateral and vertical) halo is complicated and controlled by several variables, such as differences in the mobility of elements which can be function of temperature, pressure, physicochemical specificities enclosing rock, etc.

These zonings can be classification of the use geochemical zoning, with the mineral solutions to flow instruments are matched. This can be useful as a guide in determining the direction and mineralization activity center used to be. Numerical methods in analyzing series of zoning are used in the primary halo, are:

1- Grigorian Method: Based on put data normalized data in a certain interval and compare their changes in shapes. [1]
2- Solovov method (gravity center): gravity center of halo for a two-element ratio is obtained. [1] This more comprehensive than the Gregorian method but has two problems: Effect of torque and weakness in analyzing horizons with different distances. ‘Axis level’ method was developed to correct these problems by using integral of the halo surface in Perpendicular direction of geochemical profiles. The aim of this method is effecting of halo shape to obtain the center of gravity.

This is similar to the mean value theorem in integral and led to obtain a gravity axe for vertical halo, this axe is called ‘Axe Level’. Geochemical element zoning is the result of sorting axes levels.
High pressure and temperature silicon isotope fractionation between metal and silicate

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The Si stable isotope fractionation between metal and silicate has been investigated experimentally in order to better constrain the amount of silicon present in the Earth’s core. Experiments at 1800°C were conducted at 1 GPa, while those at 2000 and 2200°C were performed at 7 GPa. All experiments were in MgO capsules so that no silicon was lost during the run and the three-isotope technique was used to demonstrate equilibrium. The isotope analyses were measured by laser ablation MC-ICPMS as spatial resolution is a key parameter in analyzing experiments.

The temperature dependent silicon isotope fractionation is

Δ30Si_{sillate-metal} = 7.45±0.41*10^{-6}/T^2 shown in the figure above, experimental data points shown in circles along with best fit line (solid) and theoretical curve (dashed, [2]). The current experiments have: 1. duplicated our previous results [1] performed in a graphite capsule (triangle in figure above), demonstrating that several weight percent carbon in iron metal does not change the silicon isotope fractionation factor, as predicted; 2. shown that the silicon stable isotope fractionation between metal and silicate is insensitive to the structure and composition of the silicate as the fractionation between silicate melt and olivine is insignificant; and 3. shown that there is no pressure effect on isotope fractionation between 1 and 7 GPa (to within analytical uncertainty).


Nature and characteristics of metasedimentary rocks in Northern Sanandaj-Sirjan Zone

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Upper Permian-Lower Trias sediments from the Sanandaj-Sirjan zone (SSZ) in western Iran record a cycle of Neotethyan oceanic basin opening and closure when the Central Iranian block separated from Gondwana and Arabia. Their studies could determine constraints of the geotectonic evolution of the area. The sediments were metamorphosed under mid-to-upper greenschist-facies conditions due to subsequent northeastward convergence of the oceanic domain below the Iran. Geochemical analysis implied that the studied metasedimentary rocks have relatively uniform chemical composition which may indicate differing from similar sedimentary rocks [1]. Davoudian et al. [2] however reported eclogite lenses from a locality near north of Shahrekord which indicate high pressure metamorphism in the SSZ and tectonic processes such as shearing leading to their exhumation during following continent–continent collision.

The granular and lepidoblastic to lepidoblastic textures are seen in the slates and phyllites, respectively. Andalusite and garnet are the major porphyroblasts in the schists. These rocks are composed of biotite, muscovite, quartz and feldspars. The schistosity of rocks is oriented in the NW-SE direction. Major element data has a narrow range and enrichment in Al2O3, all of which can be interpreted as a reflection of a pelitic provenance. It is supported by low Cr and Ti concentrations that prevent a mafic source. In addition high abundances of S-type granitoids that are penetrated into this metasedimentary country rocks reveal partial melting of metapelites to produce these felsic rocks.

Keep and touch – Dust and mineral iron utilization by the marine diazotroph *Trichodesmium*

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Oceanic blooms of *Trichodesmium*, a filamentous N$_2$ fixing cyanobacterium, provide ~50% of the new nitrogen sources to subtropical and tropical areas, fueling primary production and influencing nutrient flow and biogeochemical cycling of organic and inorganic matter. *Trichodesmium*’s extensive surface blooms require large inputs of iron that are partly supplied by aeolian dust sources. Yet the processes and mechanisms associated with dust acquisition are currently poorly defined. Here we explore how natural populations and laboratory cultures of *Trichodesmium* collect, process, and utilize iron from synthetic iron oxides and desert dust. Using a combination of uptake and dissolution experiments with microscopic observations, we find that, similar to most phytoplankton, solid-phase iron has to dissolve prior to its acquisition by *Trichodesmium*. We show that, unlike other studied phytoplankton, *Trichodesmium* apply cell-surface processes that accelerate the rate of dissolution of iron from iron oxides and mineral dust particles, and thereby increase cellular iron uptake rates. Natural puff colonies are particularly effective in dissolving dust, probably due to efficient dust trapping by the intricate colony morphology, followed by active centering and packaging of the dust within the colony core (Fig. 1). Thus, colony formation in *Trichodesmium* provides an advantageous strategy for iron acquisition from particulate sources such as dust.

An experimental study on the effect of melt composition on partitioning behavior of copper in magmatic-hydrothermal systems

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Copper is one of the major ore metals in porphyry-type deposits. It has been proposed that metals in those deposits are magmatically derived. The essential feature of the magmatic-hydrothermal model is the separation of metal-rich aqueous fluid from silicate melt. Experimental studies on the partitioning of copper between granitic melt and aqueous fluids have demonstrated the importance of complexing agents, especially chloride, in the transport of copper. However, few experimental data are available concerning the role of melt composition in magmatic-hydrothermal process.

The present study was conducted to evaluate the effect of melt composition on the partitioning behavior of copper. We investigated experimentally the fluid/melt partitioning of copper in the systems synthetic haplogranite gel-H$_2$O-HCl at 1kbar, 850 °C with Ni-NiO buffer by using rapid-quench cold seal bombs. Experimental data show that the partition coefficient of copper $D_{Cu}$ fluid/melt linearly increases with increasing HCl concentration. That agrees with results of other researchers, who interpreted this behavior as the result of the formation of CuCl complexes in the fluids. $D_{Cu}$ fluid/melt show a strong melt composition dependence, increasing from 1.28 to 10.09 with the molar (Na$_2$O+K$_2$O)/Al$_2$O$_3$ of melt varying from 1.56 to 0.83, and increasing from 1.35 to 22.18 with the molar Na/K of melt varying from 0.58 to 2.56. The data presented here suggest increasing partition of copper in peralkaline, especially K-rich, granitic melt phase. It implies that, like the fluids, the changes of melt composition also have great effects on the partitioning behavior of copper between aqueous fluids and silicate melt.

**Figure 1:** Active centering of dust by puff-shaped natural *Trichodesmium* colony, enabling it to dissolve and acquire iron from dust.
Nanoscale study of exopolymeric substance-mediated uranium biomineralization

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Bacterially-mediated biogenic reduction of soluble hexavalent uranium U(VI) into a less-soluble U(IV) product is among the planned bioremediation strategies at uranium-contaminated sites in the U.S. The primary product of this reduction is thought to be uraninite (UO₂), a highly insoluble crystalline nanoparticulate. While uraninite forms under certain conditions, recent research has shown formation of another U(IV) species under different conditions. Shewanella oneidensis MR-1, an intensely studied bacterium for its biomineralization as a function of medium. Using scanning transmission X-ray microscopy (STXM) coupled to near edge X-ray absorption fine structure (NEXAFS), we acquired wild-type and mutant each generating either UO₂ or remediation properties, produces UO₂ under simple aqueous solutions (sodium bicarbonate). In the presence of moderate or high concentrations of alkaline earth cations such as Ca²⁺, the same bacterium will form U(IV) diffusely distributed on cell biomass and biopolymers, termed monomeric U(IV) [1].

There is electron microscopy evidence that exopolymeric substances (EPS) play a role in the formation of UO₂ [2]. Moreover, EPS-deficient mutants appear to produce less UO₂ than the wild-type, confirming that prediction.

Here, we present a combined microscopic and spectroscopic approach to address the changes in U biomineralization as a function of medium. Using scanning transmission X-ray microscopy (STXM) coupled to near edge X-ray absorption fine structure (NEXAFS), we acquired carbon speciation and actinide elemental maps of Shewanella oneidensis wild-type and mutant each generating either UO₂ or monomeric U(IV). In concert, we also provide cryo-preserved, low-dose transmission electron microscope (TEM) images of the reducing bacteria thin-sectioned to display ultrastructure features. The specificity of the association of UO₂ and monomeric U(IV) with biomolecules was demonstrated with these approaches suggesting the importance of individual biomolecules in controlling biomineralization products.


Modelling the free energy of adsorption of persistent organic pollutants at clay mineral-water interfaces

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Clay minerals represent a cheap alternative for the remediation of pollutants. The clay mineral bentonite has been shown experimentally to adsorb organic pollutants [1] and heavy metal ions [2]. Here we applied computational techniques to model the adsorption of a range of organic molecules, more specifically polyhalogenated compounds (PHCs), on the clay minerals montmorillonite and pyrophyllite. Montmorillonite, a dioctahedral smectite, is the principal constituent of bentonite, while pyrophyllite is the template for all dioctahedral smectites.

The CLAYFF [3] and GAFF [4] force fields were applied to the clay surface and organic molecules, respectively. The interatomic potentials were derived using simple mixing rules and TIP3P/FS [5] water was used in solvated systems. DFT-D2 calculations using the VASP code [6] were carried out to confirm the potential model. PMF free energy calculations were undertaken using the DL_POLY_2.0 code [7]. Further free energy calculations, steered molecular dynamics, umbrella sampling and metadynamics used the PLUMED software plug-in [8].

Our results show that the simple model for the interatomic potentials had good agreement with DFT-D2 calculations. Adsorption energies for montmorillonite were dependent on the counter ions. The free energy techniques all gave comparable results. However, metadynamics was both consistently accurate and less computationally demanding than the other methods. In general, for similarly structured PHCs the adsorption energy increased with the number of chlorine substituents. Even in simple systems the differences are significant, for example the free energies of adsorption for benzene and hexachlorobenzene on the surface of pyrophyllite were -9.6 and -38.6 kJmol⁻¹, respectively.

Relationship between incidence of esophageal cancer in Maravehtapeh region (Northeast of Iran - Golestan province) and concentration of trace elements in sediments

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Esophageal cancer is one of the ten most common cancer and the eighth cause of death in the world. In Iran annually about 51,000 new cases of cancer occur. Most organs of men and women involved in is gastrointestinal tract which about 6500 cases are esophageal cancer. Since the distribution of Esophageal squamous cell cancer (esophageal cancer belt) matches loess deposits of the world which is extended from north of China to north east of Iran, Therefore, likely there is a close relationship between loess deposits and this endemic disease.

Sediment samples of study area were taken from 50 stations in ‘atrak’ river basin. Trace elements results from ICP-MS analysis in the ‘ACME’ laboratory-Canada were studied. To obtain extent of external factors (Anthropogenic impacts), ‘Enrichment factor’ and ‘Mueller’s geoaccumulation index’ was calculated which the amount of enrichment factor was mainly between 0.5-2.5 that shows concentration of elements not affected by anthropogenic factors and the amount of geoaccumulation index was between -0.5-0.5 which also shows no significant pollution. Results of Analysis of variance ‘Anova’ test which is investigated the statistical relation of formation ‘five formations in study area’ with concentration of trace elements, shows concentration of Selenium is directly related with the type of formation since with 95 percent confidence level, there is a significant difference in amount of Se in different formations especially loess deposits which have the least Se concentration. Considering that Se deficiency in body can enhance esophageal cancer risk, recommended in future studies measuring of Se concentration in water samples and blood serum of residents of this area.

Mobilization of multi-walled carbon nanotubes in consecutive imbibition and drainage events

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Carbon nanotubes (CNTs) are important engineered nanoparticles with unique and beneficial properties. As a result CNTs has been used in a wide range of commercial products including electronics, optical devices and drug delivery leading to their disposal in the natural environment. Literature studies have investigated the mobility of CNTs in saturated porous media under differing physical and chemical conditions. However, CNT transport in temporally changing porous media water content has not been investigated thus far (a common scenario with rainfall/infiltration events in the vadose zone). This study investigated the mobilization of multi-walled CNTs (MCNTs) in repeated wetting and drying cycles with varying flow rates and ionic strength of the inflow solution. Imbibition-drainage-imbibition cycle experiments suggest that MCNTs mobilization increased with increase in flow rates. MCNTs mobilization occurred only with first imbibition events at low ionic strengths however less mobilization happened for higher ionic strength inflow solution in the first imbibition cycle and additional MCNTs were found in the outflow solution in second imbibition cycle, using low ionic strength solution. This observation was likely due to the attachment forces between MCNTs and sand surface. Most of the MCNT mobilization occurred during liquid-gas interface movement with less chance of MCNTs to jump the energy barrier at higher ionic strength solution experiments. As a result less detachment of MCNTs occurred from the sand surface.
The Cl isotope composition of the mantle revisited
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Published estimates for the δ37Cl value of the mantle range from less than -3‰ to +5.7‰. We combine new data from mantle-derived materials with new chondritic and lunar data to refine the δ37Cl value of the mantle to between -0.5 and 0.0‰ (SMOC). Samples include basalts from Hawaii, Iceland and New Mexico (δ37Cl = -0.15±0.15‰, n=7), peridotites from Balmuccia, Italy (δ37Cl = -0.25±0.16‰, n=5), and Cl-bearing diamonds from Canada (-0.05‰). The δ37Cl values of our new and previously published data (Sharp et al. Nature, 2007; Science, 2010) average -0.15±0.35‰ (n=26), indistinguishable from the lowest lunar sample (δ37Cl = -0.7‰), the average of type 3 chondrites (δ37Cl = -0.5‰; Mercer et al. LPSC 2011) and evaporites (~0‰).

Although Cl isotope variations do exist in contaminated mantle (John et al. EPSL, 2010), the large published range for the primitive mantle is explained by analytical artefacts. Published TIMS data are unreliable, yielding high δ37Cl values (Nakamura et al. LPSC 2011). A published SIMS value for ‘archived’ MORB (< -3‰, Layne et al. Geol. 2009) has a Cl content an order of magnitude lower than corresponding standards, explaining the anomalously low value. Low mantle estimates from gas source mass spectrometry (Bonifacie et al. Science, 2008) are also likely artefacts of small sample size; their observed systematic decrease in δ37Cl value with size is not seen in our work, presumably because we use a more sensitive continuous-flow method. We do see a sharp drop off to δ37Cl values of < -3‰ for peak areas less than 200mV sec, but larger replicates of the same mantle samples always give δ37Cl values close to 0‰. The similarity of the crustal and mantle reservoirs explains the lack of secular variation in crustal samples, obviates the need for a fractionation mechanism between mantle and crust and defines a homogeneous inner solar system reservoir.

The Cl isotope composition of the Moon and Mars
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The bulk Earth and the least altered carbonaceous chondrites have Cl isotope compositions (δ37Cl values) close to 0‰ (Sharp et al. Nature, 2007; Mercer et al., LPSC, 2011). In contrast, Cl isotope variations on Mars, and especially the Moon, are extreme – Apollo samples range from near 0‰ (the Earth value) up to 24‰ (Sharp et al. Science, 2010 and unpublished). We interpret the high δ37Cl values as a result of degassing of metal chlorides. On Earth, Cl volatilizes from basaltic melts as HCl (g) with no apparent Cl isotope fractionation. In the absence of H2O, Cl volatilizes as metal chlorides, which leads to the preferential loss of 35Cl, and an ever-increasing δ37Cl value of the residual Cl in the melt. The δ37Cl value is a function of both the H/Cl ratio and total Cl content. The lowest and Earth-like δ37Cl value is found as surface coatings of lunar glass beads which have the highest H- and lowest Cl- contents (Saal et al. Nature, 2007) of all measured samples. The highest δ37Cl values are found in KREEP basalts (McCubbin et al. GCA in press), which formed in melts with high Cl contents. These results are consistent with a chemical divide between H and Cl. Cl is lost by HCl volatilization until either Cl or H is consumed, leaving the other element in excess. The low δ37Cl samples (74002, 36) fall on the high H/Cl side of the chemical divide, the high δ37Cl value samples lie on the low H/Cl side. If initial Cl contents are low, Cl vaporization will be minimal because Cl saturation of the melt may be only slightly overstepped. We conclude that the Moon was generally anhydrous (10s of ppb H), but anomalous eruptive samples (lunar glass beads) with high H- and low Cl-contents existed and are manifest as low δ37Cl samples.

In contrast to the Moon, Martian meteorites range from -3‰ to +2‰ (n=8). All shergottites have negative δ37Cl value and all cumulates have positive δ37Cl values. Only near-surface effects are known to fractionate Cl isotopes. The different Cl isotope compositions of Martian samples are explained by near-surface contamination or volatile loss.
Organic matter photochemistry: Singlet oxygen precursor lifetimes

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Background
Dissolved organic matter (DOM) photochemistry plays a key role in pollutant fate and carbon cycling [1, 2]. Central to this are various reactive intermediates whose production and reactions can alter the DOM. These include O2, O2, and H2O2, e (aq), OH, and triplet DOM states (3DOM*) [3]. Various evidence suggests that 3DOM* is the O2 precursor.

3DOM* + O2 → 1DOM + O2

Intersystem crossing from the excited singlet forms 3DOM* which then transfers energy to O2. Despite many studies on O2 production, the photophysical properties of 3DOM* are not well known. This work uses the O2 dependence of 1O2 quantum yields (1O2) to estimate the yields and lifetimes of 3DOM* as a function of wavelength. Experiments employed a Xe lamp, bandpass filters, and furfuryl alcohol as a 1O2 probe. Buffered D2O was used as a solvent to increase the 1O2 lifetime, allowing for extensive experimentation.

Results and Discussion
Figure 1 displays data for Suwannee River OM at 370 nm. The asymptote above 0.5 mM O2 shows that all 3DOM* precursors to 1O2 are being trapped and that their quantum yield is 0.025. The ratio of the intercept to slope of the inverse linear plot equals the lifetime of 3DOM* multiplied by the total rate constant for its quenching and energy transfer to O2. Assuming a total value of 1010 M-1 s-1 for these processes yields a 3DOM* lifetime of 6.5 µs, which is also found at 313 and 415 nm. Other samples have similar lifetimes that are also invariant with wavelength. However, the quantum yields vary by more than two-fold. This suggests that (1O2 is controlled by absolute yields of 3DOM* rather than its decay kinetics.


Dissolution-precipitation as a possible mechanism of C-O-H fluid/melt segregation in the deep mantle

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Trace amounts of fluid dispersed in the mantle cannot be easily removed from the crystalline framework if that insoluble in the fluid. However, at the mantle conditions water and carbonates are excellent silicate solvents. Hence, the migration of a fluid droplet through a solid may proceed by a combination of dissolution and deposition of the solid at the forward and rear faces of the fluid/melt droplet respectively, and solute flow across the droplet. The driving force for this process is a concentration gradient of solid silicate in the fluid. This can be caused by temperature gradient, differences in stable and metastable phase solubilities, and stress.

In this study we measured MgO-SiO2 diffusion in the K2Mg(CO3)2 (KMC), K2Mg(CO3)22H2O (KMCH), and H2O at 17 and 24 GPa. The summary of obtained data is shown in the figure below along with available literature data on diffusion in the silicate and carbonate melts and water fluid.

Based on obtained results we estimate stress driven fluid migration rate. For example, at low mantle conditions (2000 K and 25 GPa) migration rate of 10-#m inclusion of hydrous fluid estimated to be 1-2 km/y at 10 MPa stress level.
Deep crust of the Siberian craton

evidence from xenolith

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Deep-seated xenoliths hosted in kimberlite pipes (Udachnaya, Leningradskaya, Yubileynaya, Komsomolskaya, Botuobinskaya, Zapolyarnaya) from the Siberian craton include mafic and felsic garnet granulite, two-pyroxene granulites, gneisses, and amphibolite. Calculated equilibration temperatures range from 600 to 850 °C at pressures from 8 to 1.4 GPa. Garnet granulites give the highest temperatures (710 - 850 °C) and pressures (9-14 GPa) and amphibolites the lowest; felsic granulites fall between these two groups. The mafic xenoliths are picrobasaltic to basaltic in bulk chemical composition. The chondrite-normalised REE patterns for the mafic granulite xenoliths vary from flat to LREE-enriched (LaN/YbN=8.6-18.8); some have slight positive Eu-anomalies. Garnet granulite xenoliths with low REE contents and positive Eu-anomalies are interpreted as cumulates. The bulk compositions of felsic granulites and gneisses vary from andesite to rhyodacite. Zircon LAM-ICPMS dating shows several episodes in the formation of the deep crust of Siberian craton. Zircons from mafic granulites are metamorphic and have concordant ages from 1.78 to 1.97 Ga. Most zircon grains from felsic granulites are metamorphic and have concordant ages from 1.78 to 1.97 Ga. This analysis will help to determine the amount and sources of organic PM mass (in particular the importance of primary biological particles to PM), and to investigate potential impacts of naturally emitted PM on human health.

Primary biological organic particles in ambient PM in the Southeastern U.S.

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Primary biological organic particles (or bioaerosols) are released by, or composed of, biological organisms. These can include fungal spores, microbes, pollen, or other materials. Little is known about the contributions of such biological materials to ambient particulate matter (PM), though indications are that in highly vegetated regions a substantial amount of organic PM mass could be due to such sources. Large areas of natural wilderness exist in the Southeastern U.S., and even the urban areas in the region are known to be heavily impacted by biological emissions.

Therefore a field campaign was launched at one urban (Atlanta, GA) and one rural site (Yorkville, GA) in fall 2009 and spring 2010 to quantify the amount of bioaerosols in both PM2.5 and PM10-2.5. Particle mass, elemental carbon (EC), organic carbon (OC), bioaerosol fragments, and several biochemical markers (endotoxin, protein, and β-D-glucans) were measured through established and modified sampling methods. The methods and method testing will be described, and preliminary results on the contributions of bioaerosol to particle organic carbon will be provided. For example, scanning electron microscopy demonstrated that bioaerosols accounted for 60-70% of the organic carbon mass in PM10-2.5.

This analysis will help to determine the amount and sources of organic PM mass (in particular the importance of primary biological particles to PM), and to investigate potential impacts of naturally emitted PM on human health.
Proxy validation from the culturing perspective: A top down approach
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Laboratory culture experiments offer promise for proxy validation under controlled environmental conditions. Long term culture experiments for benthic foraminifera have proved useful for validation of proxy metal uptake as distribution coefficients [1]. Culture experiments have also helped discern ontogenic variation and feeding effects from environmental variations [2]. However the time and culture reservoir size required for such experiments are daunting [3].

Cultures of planktonic species offer a much more practical approach to proxy identification and validation. Small cultures can be maintained under nearly constant environmental conditions. A new instrumental method allows for the analysis of plankton cultures on a cell by cell basis [4]. Measurable differences in cell physiology occur as a function of macro and micro nutrient concentrations. Results from E. huxleyi indicate evidence for variations in the Mg incorporation into pigment porphyrins. This technology is being developed to for field-based instruments and holds promise for tracking signals through the water column as material alters prior to burial.


Genesis of platinum mineralization in gabbro-dolerites of Pay-Khoy (Russia, Nenets autonomous district)
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Platinum mineralization of dolerites of Pay-Khoy anticlinorium is superimposed on magmatic sulfide mineralization; therefore the formation record of PGE-mineralization has been reviewed by us within the framework of the genesis of sulfide mineralization at late magmatic and hydrothermal stages.

Based on the formation conditions, the PGE enrichment in Pay-Khoy gabbro-dolerites can be distinguished at: 1) isomorphic inclusions in magmatogene sulfides; 2) forming intrinsic minerals from residual fluid melt after crystallization of main sulfide minerals; 3) resedimented in the form of late chalcogenides during postmagmatic transformations. Our observations show that the highest thermal PGE form in the Pay-Khoy gabbro-dolerites represents microinclusions of platinum in sulfides. At decreasing temperature the intrinsic PGE minerals formed, predominantly palladium ones, and gradually the number of corresponding mineral phases increased.

Thus, the platinoids in Pay-Khoy gabbro-dolerites are nonuniformly distributed between three mineral associations: 1) early (magmatic) chalcopyrite-pentlandite-pyrrothine; 2) intermediate (magmatic) sulfide-telluride-sulfoarsenide; 3) late (hydrothermal) arsenide-telluride.

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Rates of oxidation in CSPV experiments involving H$_2$O-bearing mafic magmas

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A difficulty in performing experiments on near-liquidus hydrous mafic melts in gas-medium cold-seal pressure vessels (CSPV) is the tendency for H$_2$O in the fluid phase to dissociate and H$_2$ to diffuse through capsule material, leading to progressive oxidation of sample material. Consequences include premature stabilization of Fe-Ti oxide phases and commensurate deviation of the liquid line of descent toward silica enrichment. Methodologies commonly employed to mitigate the oxidation problem, not without their own drawbacks, include incorporating CH$_4$ into the pressurizing gas, limiting run duration to 24 hours, enclosing samples in Au-alloy capsules, and incorporating solid buffering assemblages to serve as indicators of $f_{O_2}$ excursion. Using the Co-Pd-O system as an $f_{O_2}$ sensor [2], we examined the rate of oxidation of basaltic andesite at 1010 °C and P$_{H_2O}$=150 MPa pressurized with a mixture of Ar and CH$_4$. Our time-series reveals that oxidation occurs at very high rates of 3-4 log units within 48h. Both the variability of $f_{O_2}$ and magnitude of dehydration-oxidation are considered unacceptable for phase equilibrium work. Incorporation of additional CH$_4$ serves only to offset the progressive oxidation trend toward a lower absolute range in $f_{O_2}$. However, incorporation of a substantial mass of Ni metal powder as an O$_2$ getter to the outer capsule successfully (a) prevents oxidation within 48h, and (b) stabilizes $f_{O_2}$ at the NNO buffer.

The chemistry of some minerals from the Shir-Kuh granitoidic batholith, South-West of Yazd, Central Iran

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The S-type granitoidic batholith of Shir-Kuh (135 Ma) which is part of central Iran is located in SE of Yazd and consists of three main granodioritic, monzogranitic and leucogranitic units. The systematic changes in the composition of plagioclase reveal that the granodiorite is a calcic core plagioclase-rich, the monzogranite a differentiated melt, and the leucogranite a late residual melt. Totally, all biotites have high Al$_{VI}$ (3.2 to 6.2 apfu) which is characteristic of peraluminous granites. The high almandine component of garnet is similar to those in other peraluminous plutons and, in particular, to the magmatic garnets. Muscovite appears as both primary and secondary-looking grains. Monazite occurs as two types of chemically crystals: monazite and brabantite [CaTh (PO$_4$)$_2$]. The observed homogeneous grains of Th and U poor monazite and tiny microcrystals of brabantite inside the apatite indicate dissolving apatite during anatexis. Little hematite (less than 10%) composition which included within restite biotite consists with the idea that the Shir-Kuh granite is generated from the sedimentary source materials contained graphite. Considering the mineral assemblages presented in the batholith, the fact that some biotite may represent restite and the mean temperature of 820°C in agreement with the zircon saturation thermometry, such liquids may have formed at a temperature 750 to 850°C by dehydration melting of biotite.

Figure 1: Rates of $f_{O_2}$ variation in basaltic-andesite

Paleosol constraints on atmospheric CO₂ levels in the Archaean and Proterozoic

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Precambrian atmospheric pCO₂ levels were previously estimated using simple thermodynamic models based upon the mineral assemblages in paleosols and BIFs [1–3]. However, thermodynamic approaches often require unreasonable or poorly constrained assumptions, and their results are highly dependent on the quality of the thermodynamic data available. In particular, re-evaluation of the paleosol thermodynamic model using more recent thermodynamic data [4] demonstrates that that approach [1] is unreliable and does not provide a significant contraint for atmospheric pCO₂ reconstruction.

As an alternative, a new model based upon paleosol mass-balance during weathering has been proposed [4]. The paleosol mass-balance model gives replicable results from multiple and widely distributed contemporaneous paleosols from the Paleoproterozoic (~2.2 Ga ago [4]) and Mesoproterozoic [4–5], and gives results that are consistent with independent proxies based on microfossils [6–7]. The pCO₂ curve generated by this method spans from 2.7–0.96 Ga ago [4, 5, 8] and indicates that: 1) late Archean and early Paleoproterozoic pCO₂ levels were similar, suggesting no significant change in response to the Great Oxidation Event; 2) from at least 2.7–1.8 Ga ago, pCO₂ levels were broadly consistent at 20–40 times pre-industrial levels; 3) between 1.8 and 1.1 Ga ago, there was a significant drop in pCO₂ to less than 10 times pre-industrial levels, coincident with a change in calcification and stromatolite abundance in the oceans. Climate model results using the paleosol-derived pCO₂ values indicate consistently equable conditions from 2.7–0.96 Ga ago and are also permissive of a Paleoproterozoic ‘snowball’ Earth event, which suggests that the paleosol mass-balance model provides a quantitatively valuable constraint on Archaean and Proterozoic pCO₂ levels.


Effect of helium on structure of SiO₂ glass probed by Raman spectroscopy

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SiO₂ glass represents a prototypical network-forming glass whose structure can be understood in terms of a continuous network of corner shared SiO₄ tetrahedra, with a high degree of intermediate range order. Numerous studies on structure and compressibility have been performed on SiO₂ glass under high pressure due to its importance as a model geological component, and an increased interest on polymorphism of glasses and liquids.

In this work, SiO₂ glass was subjected to helium in diamond anvil cell at pressures up to 20 GPa. Micro-Raman measurements were performed in the back-scattering geometry utilizing argon-ion laser excitation. Single-stage, high throughput spectrometer equipped with an EM-CCD detector were used for data collection. Comparison of the evolution of Raman bands of SiO₂ glass upon compression with and without [1, 2] helium loading strongly supports incorporation of helium in the voids of SiO₂ glass structure. This is signified by a less profound narrowing of the interfering distribution, as revealed by the spectral width of band corresponding to the symmetric bending motion of Si-O-Si linkage. Similar effect is seen in the Raman spectra of a recovered sample at ambient pressure. The shape of the corresponding Raman band is largely restored, although signs of local angular distortions remain.

The Raman results on the incorporation of helium are corroborated by a parallel x-ray diffraction study on the structure factor and compressibility [3]. Comparing these observations to the findings of other studies suggest that the effect of helium on the structure and compression of SiO₂ glass is unique. The strong effect of dissolved helium may have implications in Earth’s evolution models and is also important in interpreting the high-pressure experiments in general because helium is widely used as a pressure medium.

Partial melting and element transfer during continental subduction-zone metamorphism: Geochemical insights from leucosome within UHP eclogite in the Dabie orogen

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Mineralographic observations, elemental and isotopic analyses of major and accessory minerals as well as simultaneous in situ LA-ICPMS analyses of zircon trace elements and U-Pb isotopes were carried out on a polymineralic leucosome (rutile + garnet + phengite + epidote + kyanite + quartz) and its host UHP eclogite from the Dabie orogen. The results are integrated to decipher the partial melting of UHP eclogite and its associated mass transfer during continental subduction-zone metamorphism. Multiphase inclusions mainly containing quartz + K-feldspar + K-rich melt ± plagioclase ± other silicate/carbonate minerals were found in garnet and epidote from both the leucosome and eclogite, indicating that the leucosome-forming fluid is a hydrous melt that is rich in K, Al and Si. Oxygen isotope analyses yield temperatures of 570-700°C for quartz–garnet and quartz–kyanite pairs. The same minerals from the two rocks give nearly constant δ18O and δD values, suggesting that the hydrous melt was directly derived from in situ partial melting of the host eclogite. In comparison with the host eclogite, the leucosome is remarkably rich in phengite and epidote, indicating that the hydrous melt is associated with distinct LILE and LREE transport. Garnet and rutile in the leucosome show distinct higher contents of HREE (2.2-5.7 times) and Nb-Ta (1.8-2.0 times) than the host eclogite, indicating that these normally fluid-immobile elements are also active during partial melting of UHP eclogite. The LA-ICPMS analyses show that most zircons from the leucosome are metamorphic in origin, while the all zircons in the eclogite are residue of magmatic origin. This suggests that Zr as an incompatible element is preferentially partitioned into the partial melt. Zircon U-Pb dating gives protolith ages of 774±45 Ma for the eclogite, and metamorphic ages of 217±2 Ma and 210±2 Ma for the leucosome. Thus, the leucosome is interpreted to have formed via the partial melting of UHP eclogite during exhumation of the deeply subducted continental crust. In this regard, fluid flow and element transfer in the continental subduction zone occurred in the stage of exhumation rather than subduction.

The effects of silver nanoparticles on wastewater biofilms

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The objective of this research is to understand the potential effects of silver nanoparticles (Ag-NPs) on biological wastewater treatment processes.

Methods adopted
Molecular biology techniques (polymerase chain reaction — denaturing gradient gel electrophoresis, PCR-DGGE) were used to analyze the effects of Ag-NPs on wastewater biofilms, which reveals the response of various genera in the complex biofilm microbial community. Electron microscopy was also used to examine the uptake of Ag-NPs into the biofilms.

Results and discussion
It was found that intact wastewater biofilms were highly tolerant to Ag-NPs. With an application of 200 mg Ag/L Ag-NPs for 24 h, no significant reduction of bacteria in the biofilms was detected. PCR-DGGE studies showed that microbial susceptibility to Ag-NPs is different for each genus. For instance, sulfur oxidizing bacteria Thiothrix sp. are more sensitive to Ag-NPs than other bacteria in the biofilms. Ag-NPs are quickly sorbed to the biofilms during incubation and trapped in extracellular polymeric substances (EPS) in the biofilms. This can be an important reason for the high tolerance of wastewater biofilms to Ag-NPs. After the removal of loosely bound EPS, the viability of wastewater biofilms was reduced when treated under the same conditions (200 mg Ag/L Ag-NPs, 24 h).

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Metal complexation in hydrothermal fluids: Insights from ab initio molecular dynamics

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Complexation of metals by Cl− and HS− ligands in hydrothermal fluids is a fundamental process in the evolution of the Earth’s crust and the formation of ore deposits. Current thermodynamic models of complexation equilibria under hydrothermal conditions depend on extrapolations of experimental data using equations of state based on the Born model of solvation. Thermodynamic parameters for aqueous species are often provisional estimates based on systematic correlations between fundamental properties such as entropy, volume, ionic radius etc. Computational molecular simulations, however, can be used to test current thermodynamic models, predict metal speciation, and even estimate thermodynamic properties. For a condensed fluid, molecular dynamics simulations can be used to sample the configurational degrees of freedom in order to predict properties as a function of pressure and temperature. Simulations of dilute solutions, however, require very large systems (1000’s of atoms) and very long (> 1 ns) simulation times; such calculations are only practical by treating the atomic interactions using classical two- or three-body interatomic potentials. However, classical potentials seem to be unreliable for describing metal-ligand interactions, especially for transition metals and metalloids such as Sn2+, Au3+, Cu2+ and Cu+. ‘Ab initio molecular dynamics’ treats the molecular motions classically but the atomic interactions quantum mechanically. Although these simulations are only practical for systems with 100’s of atoms over short times (< 100 ps), they are giving fundamental new insights on metal speciation in hydrothermal fluids. Here, we describe simulations of Cu, Zn, Sn, Au, and Ni in NaCl- and HS-bearing aqueous fluids up to 350 °C. We show that predicted structures and speciation are in close agreement with experiment. Based on our simulations, we propose that the major driving force for metal complexation in hydrothermal fluids is the change in translational entropy between reactants and products. Entropies and free energies of complex formation can be estimated using thermodynamic integration and metadynamics. Applications of these techniques to Zn-Cl and Cu-Cl-HS stability constants will be presented.

Collection and determination of suspended particulate trace metals: The US GEOTRACES Intercalibration cruises

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As part of the GEOTRACES Intercalibration and Methods Development effort, we have been working to optimize techniques for the accurate and precise determination of suspended particulate trace metals (TMs) from full water column profiles in various oceanic regimes. The goal has been to determine the best particle collection and analysis methods for future GEOTRACES ocean basin sections and to carry out laboratory intercalibration to arrive at community consensus on analytical methods and results. We will present results from the Atlantic and Pacific Intercalibration cruises (IC1 and IC2; 2008-09), with a focus on the feasibility of accurate and precise determination key Geotraces TMs as well as other TMs on small volume (~10L) samples collected from rosette-mounted Go-Flo bottles. We will summarize our findings with respect to filter type, practical performance, blanks and potential artifacts such as dissolved metal adsorption. Details of the filtration methodology will be described, with an important emphasis on minimizing element-dependent particle settling artifacts and determining appropriate procedural blanks. Digestion methods for particulate samples will be evaluated and results from an interlaboratory intercalibration exercise will be presented, with a summary of ICP-MS analytical approaches. Results for samples collected using 5-10L Go-Flo bottle samples will be compared with parallel samples collected with large-volume in situ pumps.
Manganese precipitation and the removal of zinc from No Cash Creek, Keno Hills, Yukon, Canada

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No Cash Creek is a natural stream that receives water from the 500-level adit of the historic No Cash Mine (1948 to 1988). The adit discharge water and stream sediments contain elevated concentrations of Mn, Fe and Zn which decrease rapidly downstream in cascading (aerated) and additionally in a quiescent peat bog environment.

Optical microscopy showed that there were coatings around lithic grains and plant fragments in stream sediments within 600 m of the adit. EMP BSE images and element mapping of the lithic coatings show concentric bands rich in Mn and Zn (Fig. 1).

Figure 1: Mn-rich coating on a lithic grain

Initial data show that the average concentration of Mn and Zn varies within one sample with type of mineral substrate from 23 wt. % Mn and 6 wt. % Zn around pyrite to 9 wt. % Mn and 4 wt. % Zn around sphalerite. Mafic lithic fragments also have higher Mn and Zn than silicic grains. There is also considerable variation across one coating (Fig.1) from 30 to 12 wt. % Mn and 8 to 4 wt. % Zn although the Mn:Zn ratio remained constant at 3.1 (st. dev. 0.5).

Coatings around wood contain predominantly Fe with <30 wt. % Fe and <3 wt. % Zn. There is no apparent relationship between the concentration of Fe and Zn.

In conclusion, the major process removing Zn from the water of No Cash Creek is coprecipitation with or absorption on Mn-rich coatings around lithic grains.

Hotspot: The Snake River geothermal drilling project

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The Snake River Plain (Idaho, USA) represents the track of deep-seated mantle hotspot that has thinned the lithosphere and fueled the intrusion of up to 10 km of hot basaltic magma into the lower and middle crust. The heat from these intrusions, and from rhyolites formed by the basalt, drives the high heat flow and high geothermal gradients observed in deep drill holes from throughout the Snake River Plain [1-3]. Heat flow in the SRP tends to be high along the margins of the plain (80-100 mW/m²-s) and low in shallow drill holes along the axis of the plain (20-30 mW/m²-s). However, deep drill holes (>1 km) along the axis of the plain are characterized by high heat flows and high geothermal gradients below about 500 m depth [2]. This discrepancy is caused by the Snake River aquifer – a massive aquifer system that extends under the plain. Thermal gradients through the aquifer are static until the base of the aquifer is reached, then rise quickly at deeper levels in the crust. Below the aquifer along the axis of the plain, heat flow values are comparable to heat flow values along the margins of the plain or higher (75-110 mW/m²-s [2]). Bottom hole temperatures for wells along the margins of the plain near Twin Falls are typically around 30-60°C at 400-600 m depth [4] and as high as 120°C at 2800 m depth in the axial region of the plain [2].

The Snake River Geothermal Drilling Project is jointly funded by the US Department of Energy (DOE) and by International Continental Drilling Program (ICDP). Our goal is to evaluate geothermal potential in three settings: (1) the high sub-aquifer geothermal gradient associated with the intrusion of mafic magmas and the release of crustal fluids from the associated wall rocks, (2) the valley-margin settings where surface heat flow may be driven by the up-flow of hot fluids along buried caldera ring-fault complexes, and (3) in the western SRP graben. Drilling is currently in progress.

Geological characteristics of the Hukeng tungsten deposit, Jiangxi Province, South China

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Hukeng tungsten deposit, located in Wugongshan metallogenic belt in central part of Jiangxi Province, South China, is one large scale quartz vein type wolframite deposit, which is in the south margin of Hukeng granite intrusion, covering the area of 6 km².

The strata exposed in the Hukeng ore district belong to the Sinian Laohutang formation and Likeng formation, and are composed of slightly metamorphic sercite phyllite, phyllitic siltstone and phyllitic sandstone. Two groups of faults are well developed in the Hukeng ore district, NE and NW faults separately, which are all composed of silicified breccia and mylonite and control the formation of the Hukeng tungsten deposit. There developed the Hukeng muscovite granite stock (γ² 230Th) with age of 151.6±2.6 [1], where developed the wolframite-bearing quartz veins. The muscovite granites are with high content of garnet, developing silicification and greisenization generally and associated with W, Zn Bi and S mineralization. Wall rock alteration in the Hukeng deposit generally and associated with W, Zn Bi and S with high content of garnet, developing silicification and hornfelsic alteration.

In this deposit, more than 310 ore veins with WO₃ grades from 0.1% to 2.5% have been recognized. These ore veins distribute in Xinsheng’ao sector, Hukeng sector and Xijialong sector. Ore types are mainly wolframite quartz ores, wolframite-fluorite quartz ores and wolframite-sulfide quartz ores. Ore minerals in this deposit are mainly wolframite and pyrite, secondly sphalerite and chalcopyrite, with minor amounts of molybdenite, chalcolite, cubanite, bismuthinite and native bismuth. The ore textures mainly include idiomorphic texture, hypautomorphic texture and poikilitic texture, and the ore structures include massive structure, banding structure and compound structure of massive and banding. Based on cross-cutting relationships of the ore veins, mineral assemblages, paragenetic sequence and ore fabrics, the ore-forming process can be divided into three mineralization stages: quartz-wolframite stage, quartz-fluorite-wolframite stage and quartz-pyrite-sphalerite-wolframite stage.

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Experimental test of the CO self-shielding model for the early Solar System’s oxygen isotope evolution

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We designed a laboratory experiment to test the carbon monoxide self-shielding (COSS) model advanced to explain the oxygen isotope distribution in the early Solar System materials [1-3]. Our unique ‘windowless’ vacuum ultra-violet (VUV) ultra high resolution laser photodissociation and photoionization mass spectrometry is designed to mimic the solar nebular photochemistry environment and experimentally verify if the CO photodissociation at VUV wavelengths (90-110 nm) would produce the expected mass independent oxygen isotope fractionation as predicted in the recently revived self-shielding model [1-3]. This model has been invoked to explain the peculiar oxygen isotope distribution observed in early solar system materials and has a specific prediction for the Sun’s oxygen isotope composition [4], a top science priority of NASA’s GENESIS mission.

However, the first experimental test of COSS model by [5] using the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL), poses a serious question on the COSS model, although the validity of [5] were immediately challenged by [6-8]. The significance of COSS model for the early solar system warrants a second opinion with closer experimental scrutiny. If the COSS model stands the test of experimental verification, it has major implications for the origin and transport of water in the Solar System that governs the ultimate habitability of planets.

Our VUV laser system can generate 4-5 orders of magnitude higher optical resolution, with brightness more than 6 orders of magnitude greater than the broadband synchrotron light source at ALS at LBNL. This will ensure higher signal-to-noise ratios when studying weak transitions or transitions of less abundant isotopologues, such as ¹³C₁₇O. Our unique ‘windowless’ vacuum ultra-violet (VUV) ultra high resolution laser photodissociation and photoionization mass spectrometry is designed to mimic the solar nebular photochemistry environment and experimentally verify if the CO photodissociation at VUV wavelengths (90-110 nm) would produce the expected mass independent oxygen isotope fractionation as predicted in the recently revived self-shielding model [1-3]. This model has been invoked to explain the peculiar oxygen isotope distribution observed in early solar system materials and has a specific prediction for the Sun’s oxygen isotope composition [4], a top science priority of NASA’s GENESIS mission.

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Evolution mechanism of groundwater environmental factors under artificial recharge

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Research Content
In order to study the effect of artificial recharge on the groundwater quality, the mixed effect of artificial recharge water and groundwater was studied by use of mathematical simulation. The evolution of the groundwater environment and characteristics of elements was studied by analysing the correlation of different amount of recharge water, temperature, redox conditions and pH, which provided basis for environmental control in indoor simulated experiment.

Results
The artificial recharge water will not lead to catastrophe or decrease of water quality in aquifer, and it will improve water quality in aquifer to some extent. The influence sphere of temperature, redox conditions and pH in different artificial recharge conditions was determined.

Figure 1: Curve of T of recharge water vs pH and T of mixed water (Recharge water:Groundwater=6:4)

Discussion on radioactively environmental problems during phosphorite mining and processing in Longmenshan area

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Longmenshan area is the main phosphorite producing zone in Sichuan province, with abundant phosphorite resources which are mostly reservoired in strata of upper Sinian, lower Cambrian and upper Devonian. The phosphorites are neritic sedimentary deposits characterized by containing less high-grade ore, more lean ore and harmful impurities unevenly distributed. There are two major phosphorite mines in studied area: Qingping and Jinhhekou mines. And the phosphorus chemical enterprises in Sichuan province are mainly located in the Tuojiang basin.

Phosphorites, especially the marine facies phosphorites are widely distributed and strongly accumulated in uranium. Most of phosphorites have high radioactive uranium contents. Owing to phosphorite mining and processing in Longmenshan area, the Chengdu plain, especially in Tuojiang basin, has higher level in radioactive element content. The primary source tracing results show that average content of uranium in phosphorites is 31.0mg/kg, much higher than the background value, and nearly 10 times of uranium content in wall rock. And the average content of uranium in phosphate fertilizer is 20.9 mg/kg, about 7 times of that in wall rock. Phosphorite mining and processing are main causes for the high radioactive elements contents in this region.

The uranium content analysis on the main river water of Tuojiang basin, Mianyuan River and Shitingjiang River, shows that the average uranium content in water is up to 1.90 ng/ml of Mianyuan River, and 0.79 ng/ml of Shiting River. Both of the values are much higher than the average level (0.309 ng/ml) of rivers all over the world.

The uranium content study on the horizontal and vertical profile of soil in the vicinity of phosphogypsum dumps in phosphate fertilizer plant shows that phosphogypsum dumping has great impact on the soil radioactive level with uranium diffusion more than 2km width in horizontal and 50cm depth in vertical.
Pb sources of bivalves from Western Canada, Mexico and Hawaii

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Bivalves from British Columbia (Canada), Hawaii (US) and Baja California (Mexico) show human-related trace metal input that we track with Pb isotope ‘fingerprinting’.

Oysters from both Desolation Sound (BC mainland) and Barkley Sound (west coast of Vancouver Island) have relatively low Pb contents (0.05–0.22 µg g⁻¹ dry weight) with Pb isotopic signatures (²⁰⁶Pb/²⁰⁷Pb = 1.1483–1.1744) indicating large contributions from anthropogenic sources.

The Pb isotopic ratios can be explained by mixing of modern anthropogenic Pb emissions with natural Pb end-members (e.g. Coast Plutonic Complex [1]). The Pb isotopic signatures of the BC oysters are also consistent with those of BC atmospheric aerosols (recorded by lichens [2]) and road dust collected from highways in the lower BC mainland [3]. More specifically, Desolation Sound oysters have higher Pb contents and lower ²⁰⁶Pb/²⁰⁷Pb values than those from Barkley Sound. The lower ²⁰⁶Pb/²⁰⁷Pb ratio exhibited by the BC mainland oysters is attributed to contributions of anthropogenic Pb emissions from a source that is characteristically unradiogenic (low ²⁰⁶Pb/²⁰⁷Pb), potentially emissions from ore smelting in a nearby facility [4].

The Pb isotopic signature (1.1652 for ²⁰⁶Pb/²⁰⁷Pb) of Hawaiian oysters (Honolulu Harbor) is comparable to that exhibited by BC oysters, despite significantly higher Pb concentration (5.7 µg g⁻¹ dry weight). Lead contents (0.07–0.42 µg g⁻¹ dry weight) of Mexican bivalves (Baja California) are within the range of those of BC bivalves with Pb signatures (²⁰⁶Pb/²⁰⁷Pb = 1.1788–1.2088) closer to natural values.

The similarity between the Pb isotopic compositions of bivalves from BC, Hawaii and Mexico suggests comparable anthropogenic Pb sources across the NE Pacific, e.g. from unleaded motor gasoline and diesel fuel. Even with the low Pb levels found in some bivalves (e.g. BC oysters), Pb isotopes can be used to identify emissions from industrial processes and consumption of fossil fuels as important Pb sources.


Structure and petrology of the mantle beneath Hawaii constrained by seismic discontinuity imaging and mineral phase relations

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Hawaiian volcanoes has been regarded as the archetype of the surface representation of deep mantle plume. Yet, the structure and chemistry of the plume remain uncertain. Our GRT imaging of velocity discontinuities combined with phase relations studied in mineral physics provides new constraints on the structure and petrology of the mantle between 200 and 1000 km depths.

While only small topographic changes were found directly beneath Hawaii, large depth variations of the 410, 520, and 660 discontinuities were found up to 2,000 km west of Hawaii. The deepening of the 410 and 520 discontinuities are consistent with high-temperature response of the α-to-β and β-to-γ transformations due to their positive Claepyron slopes. Westward from Hawaii the 660 discontinuity changes from anomalously shallow to anomalously deep, suggesting a lateral transition from the post-spinel to a post-garnet transformation (in pyrolitic mantle) across a high temperature anomaly near the base of the transition zone. The large spatial scale of 660 topography (compared to 410) is consistent with a regional-scale boundary layer and ponding of hot material at 660-km depth.

Our images also reveal reflectors at 300 and 800 km depths and splitting of the 520 discontinuity. Splitting of the 520 discontinuity can occur if the host rock is significantly enriched with Ca and Si. The 300 discontinuity can be related to a silica transition, requiring Si-enrichment. The 800 discontinuity can be related to either the post-stishovite transformation or post-garnet transformation in an Al, Si-rich rock. Therefore, these structures indicate significant presence of non-pyrolitic components in the top 1000 km of the mantle beneath Hawaii, and the composition that is responsible for these structures is likely basaltic. Our study provides first seismic evidence for the significant existence of recycled components in the mantle beneath Hawaii.
Nature of mantle heterogeneities
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Seismic studies have revealed discontinuous changes and lateral variations in velocities at different depths in the mantle. While temperature variation is an important factor, the interpretation of some large-scale mantle structures requires compositional variation. However, the composition of the heterogeneities remains unclear (e.g. primordial or recycled).

Our high-resolution seismic GRT imaging revealed discontinuities at 300, 540, 800 km depths beneath Hawaii [1]. The silica phase transitions can explain the shallower discontinuities. The post-stishovite transition in an Al-rich rock or the post-garnet transition in a Si-rich rock can explain the deeper discontinuity. We also found splitting of the 520 discontinuity (to 520 and 540), which can be related to the exsolution of CaSiO$_3$ perovskite in a Ca-rich rock. These suggest a significant amount of recycled materials (e.g. basalt) in the upper mantle beneath Hawaii.

In the mid-mantle, Fe$^{3+}$ in perovskite [2] and Fe$^{2+}$ in ferropericlase [3] undergo high spin to low spin transitions. Although these transitions are unlikely to cause seismic discontinuities, the spin transition of Fe$^{3+}$ in perovskite may change the bulk sound speed of Al-rich heterogeneities (such as basalt) at 1700-2000 km depth, where lateral variations in bulk sound speed have been documented seismically [4].

The effects of Al in the lowermost mantle would make the perovskite-to-postperovskite boundary seismologically undetectable in pyrolite [5, 6]. Our new experiments reveal that the boundary is seismically detectable in harzburgite and basalt due to element partitioning with ferropericlase and silica, implying that the observation of the D$^\circ$ discontinuity is related to a significant presence of recycled materials in the lowermost mantle [6].

This series of studies implies that differentiated rocks (e.g. basalt) injected into the mantle by subducting slabs may exist over the entire depth range of the mantle and survive over geologic time scales.


Electrolyte ion adsorption at the hematite/water interface: A cryogenic X-ray photoelectron spectroscopy study
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Cryogenic X-ray photoelectron spectroscopy was used to probe monovalent ions (Na$^+$, K$^+$, Rb$^+$, Cs$^+$, NH$_4^+$, F$^-$, Cl$^-$, Br$^-$, I$^-$) associated to the hematite/water interface. Our findings revealed coexisting cations and anions both below and above the isoelectric point of hematite. Surface loadings tend to follow the trend in the ionic radii of both alkali metal and halide ions. Chloride loadings are largely unaffected by the identity of the associated alkali metal ion. Sodium loadings, on the other hand, considerably affected along the halide series (Fig. 1). Sorption of ammonium ion occurs by hydrogen bonding to surface hydroxyl groups, a mechanism shifting the $pK_a$ of NH$_4^+$ from 9.3 in water to 8.4 at the interface.

Figure 1: Surface loadings of electrolytes sodium (closed symbols) and halide (open symbols) ions (I=50 mM).
Geochemical study of fresh volcanic glasses from ~145Ma Shatsky Rise

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Shatsky Rise is a Late Jurassic-Early Cretaceous large oceanic plateau located in the northwestern Pacific. It consists of three major massifs: Tamu, Ori and Shirshov Massifs from southwest (older) to northeast (younger), forming along the trace of a triple junction at a mid oceanic ridge. The Rise is 1000km × 200km in size. During the IODP Exp. 324 (Sept.-Nov., 2009) five sites were drilled on Shatsky Rise, two on Tamu Massif (Sites U1347 and U1348; east flank and north flank), two on Ori Massif (Sites U1349 and U1350; summit and east flank) and one on Shirshov Massif (Site U1346; summit). Unaltered fresh volcanic glasses were sampled from all sites except for Site U1349. Glass is preserved as thin rims of lava flow margins or fragments in volcanic breccias. All glasses (115 samples) are sub-alkalic (tholeiitic) basalts, with MgO and SiO2 contents ranging from 8.5 to 5 wt% and from 48.5 to 52 wt%, respectively. Three types of magmas (normal-Ti, low-Ti and high-Nb) are identified in this study. Assuming that source of these magmas was depleted MORB source mantle [1], the trace element patterns of the normal-Ti magmas suggest that they formed at deeper depths within the garnet stability field (~3GPa), whereas the low-Ti and high-Nb magmas may have formed at shallower depths, where spinel was stable (~1 GPa). Glasses with high Nb/U from Site U1348 and high-Nb type from Site U1350 indicate that the magmas of Shatsky Rise require more than one mantle source. Deep mantle melting and multiple sources for these magmas are different from N-MORB and are important factors to constrain for genesis of Shatsky Rise.


Large regional variations in F/Cl ratios for the MORB source mantle

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Fluorine (F) and Chlorine (Cl) are highly incompatible in mantle-basalt systems (Dalou et al. 2011) and their abundances in basaltic melts are generally unaffected by solubility limits (e.g. Carroll and Webster, 1994). These features could make their abundance ratio (F/Cl) in mid-ocean ridge basalts (MORBs) a good additional tracer for elucidating how heterogeneity of the MORB source mantle has evolved. Using analytical procedures developed with a Cameca IMS 1280 at Woods Hole Oceanographic Institution, F and Cl concentrations in glasses of basaltic compositions are determined routinely with precisions of ±10% (2σ) for F and ±5% (2σ) for Cl. Based only on melt inclusion data obtained here and in literature (~220) from EPR (Siqueiros FZ, Saal et al. 2002; JdF Axial, Helo et al. 2011), MAR (17°N, FAMOUS, 23-27°N, 33°S), and Gakkel Ridge (Shaw et al. 2010), it is found that F/Cl ratios display non-overlapping clusters for regions, and subgroups of a region: F/Cl = 10±1 for MAR (17°N, 23-27°N, a subgroup of FAMOUS), consistent with the north Atlantic average value of Schilling et al. (1980). F/Cl = 5±1 for Gakkel and a subgroup of JdF, and samples from 33°S MAR and a subgroup of JdF and FAMOUS possess F/Cl=2.5±0.5. In contrast, the Siqueiros dataset display distinctly high and variable F/Cl (14 – 80). It is evident that the observed variations are not produced directly by seawater-related mechanisms, and that no single F and Cl composition can be assigned to the MORB source mantle, suggesting local as well as regional heterogeneity due to incorporation of lithologies with diverse F/Cl fractionation prehistories. It is also noticeable that the range of F/Cl in MORBs is significantly different from that for arc magmas (< 0.5, e.g. Le Voyer et al. 2010).
Effect of thickness of oceanic lithosphere on chemical composition of OIBs: Implication for origin of the South Pacific magmatism

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The northwest Pacific Ocean is known to contain a large number of Cretaceous seamounts and several oceanic plateaus and rises. These seamounts, plateaus and rises may have formed during the large-scale magmatic event in the South Pacific that is still active in the present-day French Polynesia region. Although it is unclear whether the Cretaceous seamounts and plateaus were produced by the same process that is now operate in the South Pacific, distinct isotopic signatures of the Cretaceous seamounts can be traced back to the magmas of the South Pacific, suggesting that single process has been active since the Cretaceous [1].

In order to examine the geochemical connection between the Cretaceous seamounts and present-day ocean islands, elemental ratios are determined for fluid-immobile incompatible elements (La/Yb, Nb/Zr, Ta/Zr, Th/Nb and Th/Ta). A notable geochemical feature of these ratios is a correlation between the elemental ratios and ‘relative age’ that can be an index of the thickness of lithosphere beneath hot spots. In addition, there are no systematic difference in the elemental ratios between the Cretaceous seamounts and present-day ocean islands. As the thickness of oceanic lithosphere is a function of square root of its age, these correlations suggest importance of tectonic environment to determine the chemical composition of the magmas. Other important geochemical feature is that the elemental ratios of mid-ocean ridge basalts (MORBs) from the East Pacific Rise (EPR) may not be on these trends. This observation could imply that source material of the EPR MORBs is different from that of the seamounts and islands. Since the source material of EPR MORBs can have a representative composition of upper mantle beneath the South Pacific, this difference could imply the material flow from the deep mantle. Therefore melting of mantle plume from the lower mantle, which melting condition depends on thickness of lithosphere, can be a plausible origin of the magmatism in the South Pacific.


Geochemical characteristics of black slate-hosted uranium deposits in the Okcheon Metamorphic Belt, Korea

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Carboneceous black slates in the Okcheon Metamorphic Belt of South Korea are thin beds known for their low grade U mineralization accompanying rare elements such as Ba, V, and Mo. U mineralization is distinctly concentrated in coalish slates which are imbedded in the black slates. Coalish slates show highly disturbed pattern in their texture unlike black slates, and contain quartz vein and sulfide minerals such as pyrite and pyrrhotite. Chondrite-normalized REE patterns of 36 samples for both of the rock types show that coalish slates are more enriched in HREE compared to black slate, and the total REE contents are higher in coalish slate (231 ppm) than in black slate (159 ppm). These petrographical as well as geochemical features strongly suggest that U mineralization in the black slate was related with post depositional hydrothermal activity. U also shows strongly positive correlation with V, Cu, and Mo, indicating that they were precipitated together during the hydrothermal process. Sulfur isotope compositions of black slate are low in values from -19.5 to 1.5‰, implying organic sulfur from sedimentary process, and those of coalish slate range from 7.3 to 9.0‰, possibly by metamorphism or hydrothermal process. As for carbon isotope, black slate ranges from -16.8 to -3.8‰ and coalish slate from -15.8 to -4.6‰. The wide range of carbon isotope reflects the mixture of organic carbon with calcite carbon from seawater origin. On the contrary, oxygen isotope compositions of the two rock types are narrow in range and similar to each other (14.6 to 15.5‰ for black slate and 14.9 to 18.5‰ for coalish slate), implying that oxygens are from calcite of seawater origin. Thus it seems like that the rare elements listed above would have been remobilized to participate in the formation of coalish slate after they were originally introduced to black shale under reduced condition.
Introduction of three granitoid types with different origins from ophiolitic mélange of Nain (Central Iran)

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Introduction
Mesozoic ophiolte mélange of Nain is located in Central East Iranian microcontinent. Field studies and petrography indicate presence of three types of granitoids (plagiogranites, high-K granites, and tonalites) with different origins in ophiolitic mélange of Nain. Three granitoid types are different in mineralogy and are including of: (1) Plagiogranites (containing Qtz+Pl+Amp±Prh±Chl) (Mineral abbreviations from [1]); (2) high-K granites (including of Qtz+Pl+Or+Ms+small magmatic Grt (Alm) grains); (3) tonalites that are seen as intruded dikes in the amphibolitic rocks, containing Qtz+Pl+Amp+ small metamorphic Grt (Alm-Sps) grains ±Prh.

Discussion
Plagiogranites are indicated by [2] to be originated of differentiation of primary basalt. Mineral chemistry of garnets in high-K granitoids (almandine) show they have an igneous origin formed through melting of high Ca-Al sedimentary rocks. Garnets in tonalites (almandine-spessartine) have formed by regional metamorphic processes occurred after formation of tonalites (based on Fig. 11 in [3] and Table 1). In brief, (1) plagiogranites are the final products of primary basalt differentiation, (2) high-K granites have formed through melting of sediments and (3) tonalites have been resulted by some degrees of partial melting and anatexis of their host amphibolite.

Table 1: End members percent of garnets.

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>High K-granite</th>
<th>Tonalite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrope</td>
<td>5.63</td>
<td>5.94</td>
</tr>
<tr>
<td>Almandine</td>
<td>76.07</td>
<td>75.82</td>
</tr>
<tr>
<td>Grossular</td>
<td>2.28</td>
<td>2.11</td>
</tr>
<tr>
<td>Spessartine</td>
<td>16.02</td>
<td>16.09</td>
</tr>
</tbody>
</table>


3 Ga onset of the supercontinent cycle: SCLM and crustal evidence

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A full understanding of the formation and evolution of the continents requires the use of constraints from both the subcontinental lithospheric mantle (SCLM) and crust. Significant differences exist globally between >3.2 Ga versus <3.0 Ga crust and SCLM. We propose that this time is a boundary between different geodynamic regimes on Earth and the start of the supercontinent (Wilson) cycle [1, 2].

To characterize the SCLM through time, we use geochronological studies of sulfide and silicate inclusions in diamonds from more than 20 kimberlites on 4 cratons [3]. Diamonds >3.2 Ga contain exclusively peridotitic (harzburgitic) silicate and sulfide inclusions whereas diamonds <3.0 Ga contain predominantly eclogitic silicate and sulfide inclusions. Similarly, >3.0 Ga kimberlite-borne eclogite xenoliths are largely absent in the SCLM rock record, whereas they are common thereafter.

Archean crust also records major differences across the 3.0–3.2 Ga interval. Prior to 3.2 Ga, crust grew by vertical accretion over upwelling mantle in long-lived plateaux floor of extremely depleted residual harzburgitic SCLM or via slab melting and crustal imbrication over shallow subduction zones (e.g. West Greenland) [4], whereas lateral accretion, allochthonous greenstone belt growth and calcalkaline magmatic products of mantle wedge melting emerge only after 3.2 Ga [5].

This temporal and geochemical change can perhaps best be explained as the result of a step-wise change in the tectonic style of the planet from rapid mantle convection, small plates, shallow subduction, and localized recycling >3.2 Ga, followed by large plates, deep subduction, and full upper mantle recycling <3.0 Ga. These geodynamic changes would have had profound effects on mantle depletion, crustal growth, and geochemical cycles.

Magma storage conditions of Mutnovsky volcano, Kamchatka

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Mutnovsky is a typical island-arc tholeiitic volcano, located in the southern part of the Eastern Volcanic Front of Kamchatka (Russia). This active volcano hosts a hydrothermal field, one of the largest in Kamchatka, providing an excellent example of modern interaction of magmatic and hydrothermal systems. Investigations of the magma storage conditions such as depth, temperature, volatile budget and redox state beneath Mutnovsky volcano are crucial to understand the input and the role of magmatic component in the course of magma-hydrothermal interactions. We investigated these conditions experimentally and with the help of melt inclusion study.

To evaluate the magma storage conditions, two sets of crystallization experiments at 100 and 300 MPa have been performed using the most magnesian basalt of Mutnovsky as a starting composition [1]. The mineral phenocryst assemblage of Mutnovsky basalts (Ol, Pl, CPx, and Mt) was successfully reproduced at 100 MPa (1025-1100°C, 0.5–3.5 wt.% H2O) and at 300 MPa (1000-1075°C, 1.5–5.0 wt.% H2O). The mineral phenocrysts compositions in the experimental runs and in Mutnovsky basalts were similar. Compositions of experimental residual glasses saturated with Ol+Pl+CPx+Mt assemblage reproduce well the natural liquid line of descent and confirm a genetic link between primitive and more evolved eruptive products of Mutnovsky volcano.

Olivine-hosted melt inclusions from basaltic tephra (50-55 wt.% SiO2; 4-6.5 wt.% MgO) contain 1.7-2.7 wt.% H2O and 0-180 ppm CO2. According to our experimental data on H2O-CO2 solubility in Mutnovsky basalt [1], these volatile abundances correspond to shallow depths (pressures below 110 MPa). The values of S8/S3 in melt inclusion obtained by XANES correspond to the range of log fO2 between QFM+4.9 and QFM+1.7 (QFM is quartz-faylite-magnetite buffer).

Our study confirms the presence of a shallow magma reservoir beneath Mutnovsky volcano at about 3 km depth. The phenocrysts in lavas could, however, crystallize at different depths in magmatic conduit during a polybaric crystallization (starting at least from 300 MPAs).


The generation of geochemical asymmetry in MORB around Iceland by radially symmetric plume flow under an asymmetric ridge system

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Geochemical asymmetry in Mid-Ocean Ridge Basalt (MORB) around Iceland was first recognised almost forty years ago and similar spatial patterns of MORB compositions have been reported from a number of other plume-influenced ridges. Basalts from the Kolbeinsey Ridge to the north of Iceland are depleted in incompatible trace elements and have low 87Sr/86Sr and high 143Nd/144Nd when compared with basalts from the Reykjanes Ridge to the south. Previous models that have attempted to account for this asymmetry have typically been based upon the presence of asymmetry in the compositional field, temperature field or flow field in the Icelandic plume. Here we instead propose that the geochemical asymmetry around Iceland is controlled by asymmetry in the geometry of the ridge system. The presence of such geochemical asymmetry does not require radial asymmetry in the plume composition, temperature or flow field other than that imposed by the plate spreading.

Geophysical observations indicate that the plume conduit is centred under south-eastern Iceland. If mantle flows radially in the plume head from this position, then it will arrive at the Reykjanes Ridge without passing under a fully developed spreading system and will therefore have barely been melted before it rises and melts in the corner flow under the Reykjanes Ridge. In contrast, radial plume head flow dictates that the mantle that rises and melts under the Kolbeinsey Ridge has travelled through the deep parts of the melting region under the Northern Volcanic Zone of Iceland. While only modest extents of melting may occur in the deep part of the melting region, it is likely that this melting preferentially extracts magma from enriched, fusible heterogeneities in the mantle. Therefore, the mantle rising under the Kolbeinsey Ridge may already have been stripped of an enriched geochemical signature by small extents of melting during transit under the Northern Volcanic Zone. Simple quantitative models of this depletion of mantle flowing radially in the deepest parts of the melting region are able to match the first order observations from Iceland and other plume-influenced ridges such as the Galápagos.
Analysis of thermal phases in Canaanite ceramic ‘Metallic Ware’ using FT-IR spectroscopy

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Early Bronze Age (EBA) ceramic ‘Metallic Ware’ from the North Canaan was analyzed using FT-IR spectroscopy and applying of curve fitting and second derivative techniques. The Metallic Ware is hard, highly fired pottery which resounds with a distinctive metallic ring when struck. The spectroscopic analysis is advantageous in analysis of amorphous and short-range ordered thermal phases lacking of XRD peaks. The applying the spectral analysis improves the identification of the individual phases in the composition of the pottery. The results demonstrate that the ceramic 'Metallic Ware's are composed of non-calcareous or poorly-calcareous ceramics. The spectra demonstrate that the vessels are composed mainly of meta-clay. The type of the meta-clay in the composition of the pottery is identified by the location of the main SiO stretching band using curve fitting and second derivative techniques. Most of the ceramic Metallic Ware's contain mixtures of metakaolinite and meta-smectite. The appearance of both phases, indicates that calcareous raw materials contained smectite and kaolinite, were used for manufacture of the 'Metallic Ware'. It seems that the presence of smectite in the raw material enable sintering at lower firing temperature.

Study of geochemistry, geochronology and petrogenesis of the Early Paleozoic granites in South China

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This paper shows results of petrology, geochemistry, zircons U-Pb dating and in situ Hf isotope. Geochemically, the A/CNK values have an average of 1.16; the REE compositions show higher ΣREE contents, enrichment in LREEs, depletion in Eu and REE patterns; the trace element spider diagrams are enrichment in Rb, Th, U and depletion in Ba, Sr, Nb, Ti. Zircons mostly exhibit euhedral and high Th/U values, an average of 1.08. The zircons from thirty plutons yielded rather similar U-Pb concordia ages from 436±6 Ma to 441±4 Ma, corresponding to Llandovery Epoch of Silurian. Several xenocrysts yielded the U-Pb ages around 700 Ma, implying that a breakup event took place during Neoproterozoic. In situ Lu–Hf isotopic analysis shows that all the ±Hf (t) value of zircons are negative, and their model ages (TDM2) values indicate that the Silurian granitic magma came from the recycle of Meso-Paleoproterozoic basement. Researches suggest that an intracontinental tectono-magmatic event took place during the Early Paleozoic, which is characterized by folding and thrusting, leading to crustal shortening and thickening. The high geothermal temperature from thickening crust and accumulation of producing high-heat radioactive elements will gradually soften crustal rocks and cause a partial melting, forming peraluminous granitic magma. Under the post-orogenic extensional and de-pressure condition, these granitic magma rose and emplaced in the upper crust, leading to development of S-type plutons.
Compositions of phyllosilicates from the TAG hydrothermal system at 26°N on the Mid-Atlantic Ridge as guide to subseafloor entrainment of seawater: Results from ODP Leg 158

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The TransAtlantic Geotraverse (TAG) hydrothermal system east of Mid-Atlantic Ridge at 26°N in a water depth of 3670 m is one of the largest known massive sulfide accumulations on the seafloor (2.7 million tonnes of sulfide; [1]). Anhydrite is an ideal tracer in active hydrothermal systems, but (unlike phyllosilicates) it dissolves after hydrothermal activity has ceased. Phyllosilicate compositions can provide useful constraints on sub-seafloor seawater entrainment, which supplement and extend the record in gangue. Calibrating the phyllosilicate record of fluid evolution against that of anhydrite in the TAG subseafloor may hence provide us with a useful tool in studying fluid mixing in hydrothermal stockwork zones underlying ancient volcanogenic massive sulfide deposits.

Results from trace element concentrations indicate that the paragonite patterns are fairly uniform and – compared to N-MORB – show positive Ba, U, Pb, Sr anomalies. In contrast, chlorite patterns are variable and can be divided into 3 different types: chlorite type A occurs in a breccia from the peripheral part of the upflow zone and in the deepest part of Holes 957E and 957C. Type A shows negative Sr and Ba anomalies and positive U and Pb anomalies. Chlorite type B occurs throughout Holes 957E and 957C in the central part of the mound, but is lacking in samples from the periphery of the upflow zone. Type B shows no or small Sr anomalies but positive U, Ba, and Pb anomalies. Chlorite type C occurs in alteration halos of basalt from underneath the mound. It shows no significant U anomalies, but negative Ba anomalies and large positive Pb anomalies.

The results suggest that the different chlorite pattern types relate to sub-seafloor fluid flow dynamics, which are variably dominated by (i) seawater entrainment and heating, (ii) mixing of seawater and hydrothermal fluid, and (iii) pooling and conductive cooling of hydrothermal fluids.


Ultra-depleted eclogites: Residues of TTG melting

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Eclogites from the Bellsbank diamond mines (SA) fall into categories A and B of Coleman [1]. We collected eclogites from a coarse concentrate dump from the present day production. These fall into three groups, one in A (Mg-rich) and two groups B1 (Fe-rich) and B2 (Ca-rich). They are derived from a temperature range between 850 to 1050°C (A and B1) and 1050 to 1150°C (B2). All xenoliths have exceptionally fresh and clear clinopyroxenes. REE patterns from A and B1 show the ultra-depleted character in their REE patterns which were LREE depleted in both cpx and grt. However, the LREE up to Sm were enriched in most cases disturbing the Sm-Nd system. Both phases have extremely high εH with one sample giving the highest εHf ever measured with 13753 in garnet and 6518 in cpx. Such values require a long time integrated history with very high Lu/Hf in the bulk rock. We suggest that the eclogites are derived in the early Archean from picritic to basaltic protoliths of low pressure origin, which were subsequently subducted and partially molten with not much time delay. The products of the partial melting process should be TTG melts according to experimental work (e.g. [2]). The partial melting generated the high Lu/Hf ratios in the residue which are necessary to reach such extreme high εHf values as found in our rocks. The higher temperature Group B2 eclogites have positive Eu anomalies which indicate a low pressure origin as plagioclase cumulates. These eclogites still have higher εHf as most known eclogites and may also have been involved in the partial melting process. Lu-Hf grt-cpx two-point isochrones give eruption ages around 120 Ma for samples with T > 950°C; lower-T samples give increasing ages with decreasing temperature. The Sm-Nd isotope system does not give any consistent information on the origin of the rocks because of subrecent addition of LREE to the rocks.

Active methanogenesis in the subsurface during development process

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Methanogenic biodegradation of organic matter provides us prospects of methane resource artificially generated continuously in the subsurface anaerobic condition. Unfortunately, this process is such a long period in the geological condition that human being can not wait for. However, several cases in China demonstrate methanogenesis process could be very quick.

Examples presented in this article are related to the biodegradation of heavy oil components and the significant change of the associated gas characteristics. The first example is from Liaohe depression, Bohaiwan basin. Biodegradated gases were produced widely in the west of the depression, from 1300~1600 m, with temperature ranging from 45 °C to 60 °C. Accompanied crude oil had been biodegraded heavily above 4 degree biodegradation. During producing stage less than a decade, the dryness (C_1/C_1+) of gas became higher and higher from 0.92 to 0.97. Based on material balance method, about 80 percent of producing gas should be neogenicly generated. The second example is from Songliao Basin, Northeastern China. The dry coefficient of associated natural gas increased from the beginning 85% (40 years ago) to present 95%. And content of non-hydrocarbon components, such as H_2S and CO_2, slightly increases, too. The similar trend happened in the another field, Liuzhuang field of Jinhu depression in the Subei basin, Eastern China. Differently, the dryness of associated gas has been stable at 98 %, but the stable carbon isotope ratio of CH_4 varied from -51.2 ‰ to -53.6 ‰.

All those cases demonstrate that biogenic methane could be generated in amazing rates. Once appropriate conditions provided, the interesting geomicrobes can give us whatever we want.

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Mineral chemistry of the skarn type ores from Furong Tin deposit in Hunan Province, P.R.China

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Tin in skarns forms a significant part of the total Sn resource of South China. The Furong tin polymetallic deposit in the central Nanling region, South China is dominantly composed of skarn type ores hosted in Carboniferous and Permian strata and Mesozoic A-type granitic intrusions. In this study, mineral chemistry research has been carried out on skarn ores from No. 19 ore lode using microscope and EPMA analysis, in order to constrain the tin mineralization condition of skarn in Furong deposit.

Primary skarns in Furong deposit are mainly consisting of grossular-andradite, baicalite, ferro-edenite, malayaite, and minus idocrase, wollastonite, cassiterite formed under oxidizing conditions. The garnet and ferro-edenite are characterized with high Sn concentration (0.22~0.73%), distinctly higher than those formed under reducing conditions [1]. Accordingly, the primary skarn formed under oxidizing conditions. In this case, tin dominantly occurs as Sn^4+ and entered the crystal lattices of skarn minerals.

Under the alteration of the F-, Cl- and Sn-riched ore-forming solution exsolved from biotite granite magma, the primary skarn was regressive metamorphosed to form hydrothermal minerals and ores. Along the endo-contact zones of the granite and the carbonate wallrock, the primary skarns were altered to type I ores with the association of cassiterites + plagiposite + fluorite + magnetite, which mainly related to the hydrothermal fluids exsolved from biotite granite. The association of tremolite, diopside, chlorite, sulphide, i.e. Type II ores was formed along the exo-contact zones of the biotite granite, which was significantly influenced by the fluid from wallrock.

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The impact of heavy metals concentration on soil biological properties in Kintyre Pb mining area, Jamaica

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Soil contamination with heavy metals occurs as a result of both anthropogenic and natural activities. Heavy metals could have long-term hazardous impacts on the health of soil ecosystems and adverse influences on soil biological processes. Soil microorganisms are recognized as sensors towards any natural and anthropogenic disturbance occurring in the soil ecosystem. Similarly, soil nematodes are also considered as one of the important soil biota and frequently influenced by HM contamination. The total number of nematode individuals has recently been used to investigate changes in soil biota composition in response to environmental stresses. This study was conducted within the Kintyre Pb mining area. Soil sampling plots are located in the Hope River valley, in the foothills of the Port Royal Mountains near to the Kingston. Mining was discontinued in the late 19th century, leaving a legacy of superficial tailings and crushed ore. These materials have been dispersed into the surrounding areas. HM concentrations, soil pH, soil moisture content (SM), total number of nematode individuals (TotalNem) and nematode community structure were studied. In 18 soil samples (0-10 and 10-20 cm) from 3 sampling plots located in the Hope River valley, in the foothills of the Port Royal Mountains, mining was discontinued in the late 19th century, leaving a legacy of superficial tailings and crushed ore. These materials have been dispersed into the surrounding areas. HM concentrations, soil pH, soil moisture content (SM), total number of nematode individuals (TotalNem) and nematode community structure were studied. In 18 soil samples (0-10 and 10-20 cm) from 3 sampling plots with different pollution levels (low (<100 mg/kg), moderate (300-700 mg/kg) and very high (>1000 mg/kg) concentration) were sampled in triplicate. Airdried soils samples were sieved trough 2mm mesh and HM, TotalNem, SM, pH were determined in subsamples. TotalNem was significantly lower (p<0.05) in soil samples with high concentration of HM from the soil sampling plot C than in soils with low and moderate HM content from the soil sampling plots A and B. No significant differences were observed SM and pH between soil layers and sampling plots. TotalNem patterns confirmed that the concentration of heavy metals had a significant impact on nematodes. The soil nematodes were sensitive to Pb, Cd and Zn as an indicator of soil pollution with HM and can be used within the Environmental assessment projects.

A Chinese antimony smelting site and possibility for its phytoremediation

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Anthropogenic sources such as mining operations and smelting plants are great contributors to antimony (Sb) accumulation in the environment. Sb is considered a non-essential element and is toxic to most living organisms at elevated concentrations. Chinese Sb vein-type ore deposits account for 55% of the world’s resources of Sb [1], and the country has been the global dominant in its production for over 10 decades. As a consequence, water and soil as well as fauna and flora within Sb mining and smelting areas are significantly contaminated by this metalloid and co-occurring elements [2-5]. Its anthropogenic release is mainly to the land; therefore, it is crucial to investigate the fate of Sb within the soil system in the smelting areas where its release is often very high and land needs to be cleaned up.

Discussion of results

Soils were sampled at uncultivated, cultivated and fallow farmland in the vicinity of a Sb smelter in Guangxi Zhuang, China. Topsoils at all the sites were heavily polluted by metals including Sb, Pb and As; and their concentrations were measured at 410-3330 mg·kg⁻¹, 410-3690 mg·kg⁻¹ and 200-460 mg·kg⁻¹, respectively. However, the elevated concentrations of Hg (0.11-0.30 mg·kg⁻¹) may be occurred both naturally and anthropogenically at the sites studied. This study showed that aerosol particles from Sb smelter can result in severe pollution of the local environment by toxic metals and pose a high risk via agricultural plants. Dissoluble proportion of Sb was insignificant (0.70-1.63%) compared to its deposition in the surface soils; however, water extractable amounts produced a slightly reduced germination rate on wheat seed with a lighter weight. Sb(III) adsorption on the smelting site soil was studied in order to examine its mobilization in pH changes; furthermore, to determine an optimal pH for higher Sb mobility that could facilitate plant uptake. The adsorption maximum (56 ml·g⁻¹) appeared at pH of 3, while it was 10-17 ml·g⁻¹ at pH of 6-7 which showed anion sorption may be dominant in Sb sorption onto bulk soil. It is therefore suggested that to maintain soil pH near neutral will increase Sb concentration in the soil water solution and it will enhance the feasibility of the phytoremediation.

The effect of iron-oxidizing bacteria on the stability of the gold-thiosulfate complex

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Acidophilic iron oxidising bacteria, enriched from a Rio Tinto river sample collected approximately 7 km SW of Nerva, Spain, precipitated colloidal gold when exposed to 2 μM to 20 mM Au (S₂O₃)²⁻. Growth of the consortium produced soluble ferric iron and colloidal, ferric iron-oxide mineral precipitates. A range of gold (I) thiosulfate solutions reacted with the whole cultured system and with each component system separately (i.e. bacteria, spent media, mineral precipitates) immobilized gold from solution within several hours. Transmission electron microscopy and scanning electron microscopy demonstrated that the immobilization of gold occurred differently by the three components in the microbial system. When each separate constituent was exposed to 20 mM gold: bacteria precipitated 30.78% gold in the form of 5 nm colloids concentrated along the cell envelope; the colloidal, iron-oxide minerals precipitated 26.26% gold as 5 nm colloids that reduced and replaced the acicular iron-oxide filaments extending outward from the particles; and spent media, devoid of residual organics and solid iron oxides precipitated 99.51% gold as 200 nm to 2 μm gold sulfide colloids and aggregates. In a chemical control experiment, gold did not react with soluble ferrous iron under the same experimental conditions. This suggests that stripping electrons from organic material and a role for ferric iron in destabilising the gold thiosulfate complex were critical to colloidal gold formation. Analysis of whole culture systems exposed to 2 mM gold using XANES/EXAFS demonstrated that gold (I) was immobilized and reduced to a gold sulfide and elemental gold, respectively. The direct immobilisation of gold by these iron oxidising bacteria and the indirect immobilization of gold by biologically-mediated, iron oxide precipitates suggests an active and passive role the biosphere has in influencing the mobility of gold as soluble complexes or as colloids. Understanding the biogeochemistry of gold interception and accumulation within a geologic temporal setting would provide insight into dispersal of gold in natural weathering systems where weathering of gold bearing metal sulfides occurs.

Mercury stratigraphy: A proxy for volcanogenic CO₂ buildup in Neoproterozoic snowball Earth and volcanism in the K-T transition

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Mercury tends to concentrate in sediments deposited right after major glacial events [1] as a result from leaching of volcanogenic Hg from land surface and accumulation along argillaceous sediments. Wherever geological background of Hg is negligible, its concentration in sediments may be useful for investigation of climatic changes.

Volcanism is assumed to be responsible for CO₂ build up in the atmosphere during Snowball Earth event with subsequent greenhouse effect, ice melting and cap carbonate deposition [2]. Intense volcanism witnessed the Cretaceous-Tertiary transition [3] and was, perhaps, responsible for dramatic climatic change.

We have used Hg as a proxy of volcanism intensity and CO₂ build up during snowball events in Neoproterozoic cap carbonates in NE Brazil. Localities where carbonates are in sharp – but not erosional – contact with basal diamictites (earliest stages of aftermath of glacial events) and show δ¹³C values — — — occasional — — — values — — — were analyzed. Hg contents are usually over 10 times higher than background values (<1 ngg⁻¹), occasionally reaching values > 200 ng g⁻¹. Hg contents in cap carbonates of the Sergipano Belt and Ubajara Basin are similar to those in carbonates deposited coevaly to volcanic activity elsewhere. This study supports mantle-origin for the CO₂ in cap carbonates, transferred to the atmosphere by volcanism.

In three drill-hole cores in carbonate rocks that register the K-T transition (KTB) in theParaiba Basin, NE Brazil, Hg increases (4 ngg⁻¹) in the early Danian right after the KTB. Hg spikes predating the KTB register volcanism before this transition. Hg shows stratigraphic variation sympathetic with δ¹³C and δ¹⁸O stratigraphies.

This study supports Hg stratigraphy as possible tracer of dramatic climatic changes as those in Neoproterozoic snowball Earth events and in the KTB.

The effects of road salt influx on the geochemical cycling of Woods Lake, Kalamazoo, MI

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The seasonal application of road deicing salts in densely populated areas can exacerbate eutrophication, and change the seasonal geochemical/mixing cycles of urban lakes through the gradual elevation of chloride concentrations. Elevated chloride levels in hypolimnetic waters may lead to persistent density and redox stratification (i.e. meromixis), stable anoxia in bottom waters, and a decrease in biological diversity. Therefore, the goal of this study is to examine the influence of road salt influx on the geochemical and physical mixing cycles of Woods Lake, a small, kettle lake in urban Kalamazoo, MI ($Z_{max}$ ~13 m). Water samples were collected monthly between May and July 2010, and approximately twice a month between August 2010 and March 2011 at 1 m intervals using a van Dorn sampler. Temperature, pH, conductivity, and dissolved oxygen (DO) values were obtained in situ using a YSI 650MDS/600QS multiparameter sonde. Laboratory samples were analyzed colorimetrically for $\text{Fe}^{2+}$, total alkalinity, $\Sigma \text{NH}_4^+$, $\Sigma \text{PO}_4^{3-}$, $\Sigma \text{H}_2\text{S}$, and $\text{Mn}^{2+}$, by IC for $\text{Cl}^-$ and $\text{SO}_4^{2-}$, and by ICP-OES for major ions and trace metals (Mg, Ca, K, Na, Zn, Ni, Co, Cu, and Pb). The data indicate that temperature varies seasonally in a predictable manner; typical summer and fall thermal stratification is antecedent to inverse wintertime stratification, punctuated by a transition period of thermal homogeneity (November) within the water column. However, analyses of redox sensitive species (i.e. $\text{Fe}^{2+}$, $\text{Mn}^{2+}$, $\Sigma \text{PO}_4^{3-}$, $\Sigma \text{H}_2\text{S}$, etc) show that Woods Lake displays persistent redox stratification and hypolimnetic anoxia throughout the entire sampling period. For example, maximum $\text{Fe}^{2+}$ concentrations are $>290$ $\mu$M in fall and $>250$ $\mu$M in winter below 9 m, indicative of the relative persistence and magnitude of hypolimnetic anoxia. Conductivity profiles indicate the presence of a chemocline that varies from ~8 m in the spring, summer, and fall, to ~10 m in the winter. Conductivity and CI data correlate strongly throughout the sampling period, typically with an $R^2 > 0.95$. Concentrations are more than one hundred times higher than those found in rural lakes of the same region. These data imply persistent hypolimnetic anoxia and redox stratification, presumably due to nutrient and road salt inputs, and that both fall and spring turnover events never fully reach completion.

Radiocarbon depression in aquatic foodwebs of the Colorado River, USA: Coupling between carbonate weathering and the biosphere

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The $^{14}$C content of living organisms is generally considered to be in isotopic equilibrium with the atmosphere. We measured substantial radiocarbon depression of organisms within planktonic and benthic foodwebs of Copper Basin Reservoir, a short residence-time lake at the intake to the Colorado River Aqueduct in California, USA. All levels of the foodweb, had depressed radiocarbon content with inferred ‘age’ of ca. 1100 to 1200 radiocarbon years ($\Delta^{14}$C range: -137 to -151‰, Figure 1).

We presume that ‘dead’ carbon from carbonate weathering entered into the foodweb via photosynthesis, depressing the $^{14}$C content of organisms below that of the atmosphere. A two-component mixing model incorporating carbonate weathering and atmospheric CO$_2$, shows that 15-17% of the carbon in the aquatic foodwebs of Copper Basin is derived from weathering of carbonate minerals in the Colorado River basin. Worldwide, only a few cases of radiocarbon depression have been reported for aquatic ecosystems and the degree of $^{14}$C depression in the Colorado River is much larger than that observed in the Arctic or deep ocean environments.
Geochemistry of Paleocene volcanism and oceanic island arc affinities of the Chagai Arc, Balochistan, Pakistan

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The main exposures of the Paleocene lava flows occur in an east-west trending subduction related magmatic belt known as Chagai arc in the western part of Pakistan.

The Paleocene lava flows are mainly represented by basalts (49.22-52.46 wt. % SiO2) and basaltic-andesite (52.75-53.90 wt. % SiO2). The petrochemical studies show that these are mainly medium to low-K oceanic island arc tholeiites. The trace element patterns show enrichment in LILE and depletion in HFSE relative to N-MORB. The primordial mantle-normalized trace element patterns show marked negative Nb anomalies with positive spikes on Ba and Sr which strongly confirm their island arc signatures, which is further supported by flat-slightly LREE enriched chondrite-normalized REE patterns. These volcanics have lower average 87Sr/86Sr ratio (0.70446), which is more consistent with a depleted mantle source and closely correlate with oceanic island arcs rather than analogous rocks of the continental margins type arcs.

Eruptive history and chemical evolution of the Acigöl volcanic field, central Anatolia, Turkey, based on geochemical and isotopic (Sr-Nd-Pb, δ18O) constraints and ion microprobe zircon analysis

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The Acigöl volcanic field has been interpreted as a thermally growing system, where smaller magma pulses coalesced into a large, interconnected silicic magma reservoir [1]. We established a high temporal resolution chronostatigraphic framework for rhyolitic volcanism at Acigöl from zircon U-Th disequilibrium and (U-Th)/He dating combined with thermometry and O-Sr-Nd-Pb isotopic data. In contrast to previous dating [2], we found that zircon crystallized in only two pulses corresponding to separate eruptions in the eastern and western Acigöl field during Mid- (~150–200 ka, group I) and Late Pleistocene (~20–25 ka, group II) times, respectively. For group II zircons, resolvable differences exist between interior (average: 30.7±0.9 ka; 1σ error) and rim (21.9±1.3 ka) crystallization ages. These translate into radial crystal growth rates of ~10⁻¹³ – 10⁻¹⁴ cm/s. Rim crystallization ages and (U-Th)/He eruption ages (24.2±0.4 ka) overlap within age uncertainty. Compositionally, group I lavas are less evolved (SiO₂ = 71–73 wt.%), than group II lavas (SiO₂ = 74–75 wt.%). Within each group, compositional variability is small, and Nd-Pb isotope ratios are fairly homogeneous. Group II rhyolites have δ18O(zircon) overlapping mantle values (5.56 ± 0.16 ‰), whereas group I rhyolites are slightly more enriched in 18O, consistent with some crustal material input. By contrast, group II rhyolites have markedly more radiogenic 87Sr/86Sr ratios (0.7065–0.7091) compared to those of group I (0.7059–0.7065). The correlation between hydration (loss on ignition data) and 87Sr/86Sr in the group II lavas indicates that Sr was added during post-eruption alteration by wind-blown material. Isotope constraints preclude the possibility that the rhyolite magmas formed by partial melting of any known regional crystalline basement rocks. Despite the longevity of rhyolite volcanism at Acigöl, and trends from group I to group II rhyolites of progressive depletion in compatible trace elements and decreasing zircon saturation temperatures, evidence for brief zircon residence is consistent with autochthonous crystallization in small discrete magma batches rather than in a fully interconnected magma reservoir.

Molybdenum isotope fractionation during soil formation: A new proxy?

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Over the last decade molybdenum has become one of the most investigated tracers for redox conditions in the oceans. However, little is known about the processes controlling the isotope composition of the riverine inputs to the oceans. Several recent studies [1, 2] have shown that many river waters have a heavy Mo isotopic composition. However, crustal rocks are in general close to zero and therefore fractionation of Mo isotopes must occur during weathering or transport. This study has investigated the behavior of Mo isotopes under different weathering conditions. Results from a soil climate gradient from Hawaii show that redox conditions during soil formation can control Mo isotope compositions in soils. Reducing soil profiles have light isotope compositions whereas oxidizing profiles are heavy. This general isotope behavior is confirmed by results from soil profiles from Iceland. Here reducing layers within the profiles show marked negative isotope excursions. In general oxic profiles show positive isotope compositions increasing with depth and organic C content. In addition these profiles show that fractionation relative to the source rock is dependent on the degree of weathering, i.e. relatively un-weathered profiles do not show isotope fractionation. Sequential extractions confirm that organic matter plays a crucial role in fractionating molybdenum isotopes in soils. These observations together with the generally heavy isotope composition of rivers indicate that the current mass balance of molybdenum in Earth surface processes might not be in steady-state. In addition, our data open interesting possibilities for the use of molybdenum isotopes as a paleo-proxy for soil processes. Finally, our data show that interpretations of the marine sedimentary record are difficult as long as we do not understand changes in the molybdenum input over time.


Diamond anvil cell applied to the geochemistry of Earth’s core formation

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The abundances of siderophile elements in the Earth’s mantle bear the imprint of the core formation in the early Earth. Thermodynamic expressions used to constrain the metal-silicate partitioning behavior of siderophile elements are mainly established from large volume press experiments that do not cover the full range of potential P-T conditions for core-mantle equilibrium. The diamond anvil cell is the only static technique capable of achieving required P-T conditions but until now its capabilities to perform quantitative metal-silicate partitioning experiments at extreme conditions has been untapped. We use protocols that effectively link high P-T diamond anvil cell with analytical techniques such as focused ion beam device (FIB); NanoSIMS; electron microprobe; transmission electron microscopes; and in situ synchrotron X-ray diffraction measurements allow us to obtain quantitative data on element partitioning at superliquidus conditions above 30 GPa and 3000 K. Here we present our advances in both experimental and analytical methods. We look at the partitioning of 6 siderophile elements (Ni, Co, Cr, V, Mn, and Nb) that have been extensively studied at lower P-T conditions and constrain the solubility of light elements (Si and O) at these extreme conditions. Experiments were conducted between 35-75 GPa and 3100-4400 K. We then update expressions that describe the partitioning behavior of these elements to address the validity of proposed core formation models (i.e. single-stage core formation model and continuous core formation model).
Ore processing and metallurgy technologies applied to soil washing: Feasibility studies in the Linares area (Andalucía, Spain)

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For centuries, an important mining industry was developed in the area of Linares (Andalucía, Spain). This activity produced a large quantity of waste materials, which were accumulated in the surrounding of the exploitation and ore processing sites, affecting the quality of several Ha. of soil [1]. In this work, we have assessed the viability of physical separation of toxic elements, given that soil washing is a suitable remediation technique to reduce the volume of contaminated soil [2, 3]. On this purpose, we have conducted a feasibility study by means of chemical analyses, and a detailed edaphic and mineralogic characterization of the soils, followed by grain-size, gravimetric, and magnetic separation pilot-scale tests.

Chemical analyses revealed anomalous concentrations of Sb, Cu, Ag, Cd, Mn, Pb and Zn, exceeding both natural backgrounds and the maximum levels permitted by Spanish environmental laws. In this context, we propose an approach based on similar ore processing and metallurgy strategies to those used in the past to recover Pb and other metals in the study area [4]. Thus, wherever geochemical data indicated that the contaminants are predominantly present as free minerals (areas mainly related with mining waste), a treatment by means of chemical analyses, and a detailed edaphic and mineralogic characterization of the soils, followed by grain-size, gravimetric, and magnetic separation pilot-scale tests.

For example, nearly all natural soils characterised by correlations between mass losses around 125 °C and 525 °C with high coefficient of determination (0.7 – 0.9). This correlation can easily be explained by the long term influence of clay minerals on water sorption (mass losses around 125 °C) and on accumulated of humic substances [2] (mass losses around 525 °C). In contrast, CSS are usually a result of shorter time periods or prevalence of non biotic processes. Additional water binding by plant residues can modify mass losses around 125 °C and disturb the correlation. At 525 °C the decay of black carbon has a similar effect.

Further investigations should clarify to what extent the correlations found in natural soils can be used to distinguish soils from carbon containing substrates and to detect influences of cultivation, fertilization and other land use technologies.


Thermal stability of soils and the detection of use-induced changes

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Several investigations on soils are currently focused on sustainable land use. However, there are still no common laboratory method to distinguish soils from carbon containing substrates (CSS). This makes the detection and evaluation of use-induced soil changes not easy.

We tried to fingerprint natural soils using thermogravimetry. The goal was to create a reference base for easier detection of use-induced soil changes with a simple detection method. For this purpose, over 150 samples under natural vegetation were collected and analysed from natural parks, biosphere reserves and other protected regions in US, Europe, South America and Russia.

Using different statistical approaches, it was not possible to directly derive common characteristics of natural soils from peaks or curves from thermogravimetric data.

But, the thermal mass loss allows a reliable detection of organic carbon, nitrogen, clay and carbonates in soils with high accuracy [1]. Further, typical relationships were found to exist between mass losses in distinct temperature areas in soils under natural vegetation.

For example, nearly all natural soils characterised by a correlation between mass losses around 125 °C and 525 °C with high coefficient of determination (0.7 – 0.9). This correlation can easily be explained by the long term influence of clay minerals on water sorption (mass losses around 125 °C) and on accumulated of humic substances [2] (mass losses around 525 °C). In contrast, CSS are usually a result of shorter time periods or prevalence of non biotic processes. Additional water binding by plant residues can modify mass losses around 125 °C and disturb the correlation. At 525 °C the decay of black carbon has a similar effect.

Further investigations should clarify to what extent the correlations found in natural soils can be used to distinguish soils from carbon containing substrates and to detect influences of cultivation, fertilization and other land use technologies.

Analysis of organic biomarkers in single Precambrian oil-bearing fluid inclusions using ToF-SIMS

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Organic biomarkers are valuable sources of information on the biodiversity and environment of early Earth. However, with organic biomarkers, especially in old samples, there are often problems of syngeneity and many of the most ancient biomarkers are suspected of being younger contamination.

A type of sample where biomarkers are better constrained in the rock is oil-bearing fluid inclusions, especially if single inclusions can be analysed. However, most inclusions, including Precambrian oil-bearing fluid inclusions are so small (less than 10 µm) that analyzing single ones with conventional techniques is not possible. Therefore, we have developed an approach employing time-of-flight secondary ion mass spectrometry (ToF-SIMS) to selectively open individual oil-bearing inclusions by C_{60}^{+} ion etching, and to subsequently analyse their content. Using this approach steranes and hopanes could be detected in single Ordovician oil-bearing inclusions (15-30 µm) from the Siljan impact structure in Sweden.

Now the developed approach has been applied on Precambrian samples. Four different oil-bearing fluid inclusions trapped in a 1.43 Ga sandstone from the Roper Superbasin in Australia were opened and analysed with ToF-SIMS. The ToF-SIMS spectra of the oil in the different inclusions were similar to each other indicating that the same oil was trapped in all inclusions. In addition, the ToF-SIMS spectra contained peaks that could be assigned to alkanes, cycloalkanes, aromatic moieties, steranes and hopanes.

With further development and if applied on other Precambrian samples this approach could help answering questions regarding early evolution of life on Earth.

The impact associated to wastewaters treatment plant discharges into a fluvial system (Central Portugal)

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The Ocreza River is an important fluvial system in inner central Portugal, which originates in the Gardunha Chain at 1160 meters high and stretching for about 80 km before flowing into the Tagus river. It has several creeks and tributaries along which there are several communities dedicated mostly to agriculture and livestock activities. The impact of several wastewaters treatment plants discharges on water quality must be characterized, monitored and, mostly controlled as it has a crucial role on local communities’ welfare.

This paper focuses on the Alcains and Castelo Branco wastewaters treatment plants which discharges into the Líria River, an Ocreza’s tributary. Twenty georeferenced water samples were collected between the wastewaters treatment plants discharges and the Ocreza river confluence. Secondary inflows were identified and sampling performed at approximately equal distances and, were conducted during three different hydrological periods in 2010: rainy winter (January), intermediate conditions (March) and dry season (June). The following chemical parameters were analyzed: biochemical oxygen demand (BOD), dissolved oxygen concentration (DO), dry residue, P total, N total; pH, temperature and microbiological parameters. The dissolved oxygen concentration (DO), biochemical oxygen demand (BOD) and microbiological parameters were used as indicators to the presence of organic matter in the body of water, and consequently as parameters for evaluating the environmental pollution.

The QUAL2kw software was used to construct a water quality model performing a coupled hydrodynamic and water dispersion model to simulate the pollution in the Ocreza River due to sewage effluent. The model’s fair calibration is demonstrated by the simulation consistent results with field observations and demonstrate that the model has been correctly calibrated. The model is suitable for evaluating the environmental impact of sewage effluent on Ocreza River from the wastewaters treatment plant inflows, allowing feasibility studies of different treatment schemes and the development of specific monitoring activities.
Recognition of mucilage and microbial events on the Early–Late Pliensbachian (Lusitanian Basin, Portugal)

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In the Lusitanian Basin (Portugal), the Early–Late Pliensbachian interval (c. a. 186 Ma, Early Jurassic) is characterized by the deposition of organic-rich marl–limestone hemipelagic alternations on a north-westerly dipping low-energy carbonate ramp [1]. The aim of this work is to present the characterization of these organic-rich facies at a basinal scale, supported by the combination of Sedimentology, Stratigraphy and Paleontology with Geochemistry, Organic Petrography, Palynofacies and Biochemistry.

Several well defined black shales (s. l.) are observed throughout the studied sections, where TOC values reach up to 26.3 wt.%. From the integration of the available data, we suggest that these black shales correspond to mucilageneous aggregates and/or microbial biofilm events, whose origin is related with palaeoceanographic and palaeoclimatic changes. Modern and fossil examples show that massive mucilage and microbial outbreaks can have severe effects on the biota [e.g. 2, 3] and that their preservation can be an important factor in influencing several elemental cycles and their major disturbances [e.g. 4].

It has been evoked that the Late Pliensbachian corresponds to a widespread organic matter preservation interval (Late Pliensbachian OMPI), linked to the complex chain of events that ultimately led to the Toarcian Oceanic Anoxic Event [1]. Our data highlights the relationship between microbial development and contemporaneous palaeoenvironmental changes and adds valuable information to understand their role in the modern world.

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

The interaction between Central and South America from Sr-isotope chemostratigraphy of Cenozoic coral reef successions

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The interaction between Central America and South America has been extensively studied due to important implications that the separation of the Caribbean and Pacific oceans may have in terms of oceanography, ecology (i.e. connectivity) and global climate. Timing the exact closure of the Panama Isthmus has remained difficult due to the lack of a well-constrained chemostratigraphic framework for the Panamanian-Colombian area. The Panama Basin is the main tectonic feature separating the Chorotega and Choco-Darien Blocks [1]. Previous investigations have suggested a connection between western Panama and North America at ca 19 Ma; implying disconnection between the Chorotega and Choco-Darien during that time [2]. However, recent geochronologic investigations along eastern and western Panama have suggested a tectonic interaction between Central America – South America at ca 23 Ma [3, 4].

The Darien Formation in the Choco-Darien Block consists of Eocene-Oligocene collisional arc-related volcanics. Exquisitely well-preserved coral reef patchy carbonate successions nonconformably overlay the Darien Formation. Sr-isotope chemostratigraphic data and calcareous nanoplankton suggests a depositional age between 23.3 and 13.65 Ma. The depositional age of such carbonate successions that cover the latest arc record in eastern Panama provides a unique temporal framework for the beginning of Panama-Northern South America tectonic interaction and the resulting Cenozoic paleoceanographic, paleoclimatic and paleobiologic changes in the neotropics.

[4] Montes et al. (Submitted)
Novel denitrifier method for measuring $^{15}$N and $^{18}$O of nitrate

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The ‘Denitrifier Method’ using *Pseudomonas aureofaciens* to convert NO$_2^-$ and NO$_3^-$ quantitatively to N$_2$O, first devised by Sigman & Casciotti et al. [1, 2] has become a state-of-the-art method for nitrate preparation prior to IRMS analysis of $^{15}$N & $^{18}$O. This method is, however, relatively laborious and requires numerous successive steps of culturing, purging and concentration, all of which increase the risk of contamination by non-sample NO$_3^-$ or N$_2$O. Moreover, the viability of the used *P. aureofaciens* cultures typically remains unreported, making it difficult to assess fractionation biases through incomplete NO$_2^-$ and NO$_3^-$ conversion. Here we present a novel denitrifier method that uses *Paracoccus denitrificans* (a complete denitrifier) to remove any NO$_3^-$ and N$_2$O background from the growth medium before culturing *P. aureofaciens*. We found that *P. aureofaciens* cultures growing oxically in sterilized *P. denitrificans* treated medium can be switched successfully to anoxic respiration in the presence of 20 mM NH$_4^+$ with the sample NO$_2^-$ and NO$_3^-$ as the sole electron acceptor. This significantly shortens preparation times and reduces the risk of contamination (Tab. 1). We successfully tested the method for water samples with pH as low as 4 and for soil extracts containing 0.5 M KCl. First results applying the novel method to pore water samples from an N-saturated subtropical forest in southwest China will be presented.

<table>
<thead>
<tr>
<th>Precision (nmol)</th>
<th>$^{15}$N accuracy (%)</th>
<th>$^{18}$O accuracy (%)</th>
<th>Duration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>20</td>
<td>0.4</td>
<td>20</td>
</tr>
<tr>
<td>New</td>
<td>≤ 25</td>
<td>1.9</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Table 1: Comparison of the original with the newly developed denitrifier method


Large sulfur isotope fractionation does not require disproportionation

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Microbial sulfate reduction (MSR) controls the partitioning of sulfur isotopes among various sulfur reservoirs, leaving a sedimentary sulfur isotope record that is used to track the oceanic budgets of oxidants, the progressive oxygenation of Earth’s surface, and the evolution of microbial metabolisms through geologic history. Although previous environmental studies and models suspected that MSR alone could produce sulfur isotope offset between sedimentary sulfides and sulfates as large as ~ 75‰, all culture studies to date reported enrichment factors for MSR ($^{34}$S) smaller than 47‰. $^{34}$S fractionation larger than 47‰ and its relationship to $^{33}$S fractionation ($^{33}$λ) were thus thought to indicate active microbial disproportionation and oxidative recycling of sulfur. A pure, actively growing culture of the recently isolated marine sulfate reducing bacterium (DMSS-1) produces sulfide depleted in $^{34}$S by 6 to 66‰. The largest isotope effects occur during the very slow growth of cultures grown on glucose, a recalcitrant organic substrate. The large isotope effects and the associated $^{33}$λ values produced by DMSS-1 during sulfate reduction approach the equilibrium value between sulfate and sulfide at low temperatures (<40 °C). These findings bridge the long-standing discrepancy between the upper limit for $^{34}$ε in laboratory cultures and the corresponding observations in nature and indicate that near-equilibrium $^{34}$ε and $^{33}$λ do not unambiguously record the stepwise oxygenation of Earth’s surface environment. Instead, the strong dependence of $^{34}$ε on the availability and quality of natural organic matter suggests that temporal or regional changes in the sulfur isotope systematics may reflect the changing nature of organic material that fueled sulfate reduction during the Proterozoic and the Phanerozoic.
Iron distribution in the clay of weathering crust of Katalambinskoe ore field

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Samples of the so-called structureless clays from mature weathering crust of Katalambinskoe ore field have been studied. Kaolinized white clay and ocher brown clay characterized using infrared (IR), EPR and Mössbauer spectroscopy. X-ray diffraction (XRD) study indicates that raw materials consists of low-ordered kaolinite (up to 70%), well-ordered muskovite and minor relics of initial chlorite. Major impurities in ocher clay are goethite, lepidocrocite, magnetite and uncrystallized iron oxide.

Kaolinite substituted muscovite and paragonite in the initial rocks. IR spectra in the region of stretching vibrations of OH groups are also indicated presence of structurally imperfect kaolinite. Chemical analysis of the kaolinizated sample show content Fe₂O₃ = 3.10%, FeO = 0.35%, in ocher sample - Fe₂O₃ = 20.64% and FeO = 0.44%, respectively.

Mössbauer spectrum of white kaolinizated clay can be described by a superposition of two doublet of three- and ferrous iron. According to [1], the doublet can be attributed to the octahedral position of ferric iron in the kaolinite structure. High linewidth of the doublet of ferric iron indicates a low ordering kaolinite. Ferrous doublet has parameters typical of octahedral cis- positions in muscovite present in the samples according to the x-ray analysis. It accounts for about 15% of the total iron content in the sample.

Sextet structure shows the presence in the brown clay of the two magnetically ordered phases, characterized by the values of magnetic hyperfine fields 500 and 470 kOe. It should be noted that the doublet spectrum can be observed in goethite, if present by nanoscale particles. According to X-ray analysis is goethite is the dominant Fe-containing phase. Detectable Ta concentrations range from 0.001 to 0.003 ppm. Niobium concentrations range from 0.02 to 0.24 ppm in Spruce twigs, 0.005 to 0.071 ppm in Spruce needles (dry weight normalized), and 0.012 ppm to 0.030 ppm in Fir needles (dry weight normalized).

Spruce twig data show a positive correlation between Fe, REE and Zr; Nb correlates positively with Fe, Ti, Ce, and Nd. Fir twig data were not analysed. Spruce needle data suggest strong positive correlations between P, Mg and Ti, as well as Nb and REE, and Zr and Fe, and a moderate positive correlation exists between P and Ca. There are not enough Fir needle samples for formal statistical analysis, however, strong positive correlations are suspected between Fe and REE, Fe and Ti, and P and Zr.


Biogeochemical footprint of the Ta-, and Nb-bearing carbonatite, Blue River Area, British Columbia, Canada

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This orientation survey demonstrates that coniferous trees are suitable sampling media in the exploration for carbonatites and related rare earth elements (REE), Ta, Nb, and phosphate deposits.

Twenty four samples of twigs with needles from Subalpine Fir (Fir) and White Spruce (Spruce) were collected over the Upper Fir carbonatite and surrounding amphibolites and paragneisses. Twigs and needles were analyzed separately. Twigs were milled using a Wiley mill. The resulting pulps were digested in HNO₃, then Aqua Regia and then analyzed by ICP-MS/ICP-ES. Needles were ashed, digested in Aqua Regia and then submitted for ICP-MS/ICP-ES analysis.

Light rare earth elements (LREE), Y, Zr and P in both twigs and needles are good exploration vectors for carbonatite-related REE and apatite mineralization. The highest concentrations of LREE are detected directly over carbonatites or fenites. Concentrations of heavy rare earth elements (HREE) are near or below the detection limit. Tantalum is found in detectable concentrations only in spruce twig samples spatially related to carbonatite. Detectable Ta concentrations range from 0.001 to 0.003 ppm. Niobium concentrations range from 0.02 to 0.24 ppm in Spruce twigs, 0.005 to 0.071 ppm in Spruce needles (dry weight normalized), and 0.012 ppm to 0.030 ppm in Fir needles (dry weight normalized).

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Rare Earth Elements (REE) recovery as a by-product of fertilizer production from sedimentary Phosphate deposits – Conceptual evaluation

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Worldwide, phosphate deposits are classified into three main categories: a) phosphorites (sedimentary phosphate deposits), b) apatite-rich igneous rocks and related residual deposits, and c) modern and ancient guano accumulations. Marine phosphorites are the most significant in terms of global phosphate production, reserves and resources. Phosphorites average approximately 460 ppm total rare earth elements (ΣREE), are enriched in REE relative to typical shale (207 ppm ΣREE), and can contain more than 1600 ppm ΣREE. Total concentration and proportions of individual REEs within phosphorites vary substantially.

Currently, China produces the vast majority of the world’s REE supply. Rapid increases in internal demand for REE have motivated the Chinese government to introduce limits and taxes on REE exports. The resulting insecurity regarding global REE supply created a rise in REE prices. The world’s REE demand for 2010 was estimated at 125 000 tonnes. Assuming average REE content of 460 ppm ΣREE in phosphorite, the world’s phosphate production of 170 million tonnes represents over 70 000 tonnes of contained REE. Considering the phosphorites of the Fernie Formation in British Columbia (Canada), at current REE prices, a tonne of phosphate rock has an ‘in the ground value’ of more than US$ 160. This is more than the current market value of high-quality commercial phosphorite concentrate (approximately US$ 130-150). The above rudimentary considerations indicate that at current REE prices, the economic viability of REE recovery as a by-product of phosphate mining should be re-evaluated.

In situ SXRF determination of trace element abundances in aqueous fluid at 1 - 3 GPa and 300 – 500°C: Applications to subduction zone element cycling

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Interpreting trace-element variability in arc magmas that are hypothesized to have an aqueous fluid signature is predicated on having a quantitative understanding of the aqueous fluid-mediated trace-element transfer at PT conditions attending slab-sediment devolatilization. Experimental efforts to quantify the element-scavenging potential of aqueous fluid (s) were historically performed ex situ by recovery-type experiments. Here, we report further development of a synchrotron-based hydrothermal diamond anvil cell technique that allows in situ quantitative determination of trace element abundances in aqueous fluid at PT conditions appropriate for slab devolatilization. Notably, in situ reversals can be performed. The technique was developed by measuring the dissolution of YPO4 (xenotime), a proxy for the behavior of heavy rare earth elements (HREE), in aqueous fluid at 1 to 3 GPa and 300 to 500°C. Yttrium concentrations and pressure were measured in situ by using synchrotron X-ray fluorescence (SXRF) and X-ray diffraction (XRD) of gold, respectively. Yttrium standards were measured in the same sample chamber as xenotime experiments, and a multi-point standard calibration curve was used to calculate Y abundances in the fluid in the xenotime dissolution experiments. This ensures a constant fluorescence excitation volume for the standards and the unknowns. The new data indicate that Y (HREE) concentrations in aqueous fluid are relatively constant at 300 to 500°C and 1 to 3 GPa, suggesting that increasing temperature, at a given pressure, does not increase the HREE-scavenging ability of aqueous fluid. These data have important implications for HREE recycling in subduction zone environments.
Balancing of geological acidity and buffering potentials of Mid German lignite open casts by long-term experiments

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Problem and Solution

Open cast lignite mining induces sulphide weathering associated with Acid Mine Drainage - phenomena (mobilisation of acidity, sulphate, heavy metals). This partial weathering of sulphides is embedded in hydro-geochemical buffering reactions. Essential buffers are carbonates, aluminium/iron hydroxides and aluminium silicates. Especially the carbonate buffering is important [1].

For sustainable strategic activities to reduce the acidification of ground waters by the lignite dump sites Peres and Schleenhain (Germany, South of Leipzig/Saxony), it is essential to evaluate the acidification and buffer potentials of the overburden units. These investigations need to consider the applied mining technology [2].

In long-term experiments (>500d), wet samples of forefield drillings of the five aquifers and some aquiclude units were exposed to weathering (T = 10 °C).

These tests show clearly that the Oligocene aquifers (Aquifer 2 and 3) are the main problem sediments. The low pH values are coupled to a high acidity, iron and sulphate release. In contrast the glacial marly till contributes by buffering carbonates.

The subsequent buffering tests with aquifer 2 and 3 material in combination with the glacial till sediments, shows a clear effective buffering with increasing addition of glacial till. A release of iron and heavy metals can be completely prevented for longer times. The detailed investigation of the already existing water phase of the dump site Peres confirms the buffering effect by these carbonates.

Therefore the overburden dumping technology will be even more directed to the effective buffering by mixing the problematic materials with the buffering tills.


Ca isotopes of Central American arc basalts lack carbonate component

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Subduction of sediment fundamentally represents a loss of continental crust and a gain of relatively enriched components to the mantle. Provided that possible mixing end members can be defined, stable Ca isotope signatures provide a powerful probe for identifying various sources in volcanic arc magmas. For example, marine carbonates are enriched in light Ca isotopes by about -0.2 to > -1.0‰ [1], relative to igneous rocks and should clearly implicate subducted sediment. Here we present Ca isotopic compositions for basalts from along the active Central American volcanic arc front that represent the range of trace element signatures indicative of various amounts of sediment recycling through the subduction zone (e.g. based on Ba/La values).

In an attempt to balance sedimentary input and arc volcanic output across the Nicaraguan margin [2] compared sediment input (i.e. high Ba/La) in arc magmas to offshore sedimentary drill cores, concluding that over the last ~20 Ma as much as 75% of the modern sedimentary column has been subducted. Despite measuring samples with trace element signatures that imply large amounts of subducted carbonate, we find no resolvable evidence for a low ⁴⁴Ca/⁴⁰Ca component. In detail, arc basalts from Guatemala, Honduras, and Nicaragua range from 0.04 to -0.18‰ in ⁴⁴Ca/⁴⁰Ca (mantle=0 scale). These nearly indistinguishable results are somewhat surprising given the fact that CaCO₃ has 3 times more Ca than the basalts. Mass balance shows that ~2-10% carbonate should produce resolvable effects.

Several potential reasons for the missing Ca isotopic signal are considered, including that: (1) subducted carbonate has an isotopic composition similar to mantle Ca, cf. [1], (2) subducted carbonate is largely dolomite, and/or (3) the record found in the drill cores is not representative of subducted sediment in the modern arc. Our new Ca isotope data imply that, at least for the Nicaraguan volcanic arc, trace element geochemistry may be less well understood than we believe. This is supported by the fact that the highest δ¹⁸O values are associated with low Ba/La [3], and not the high Ba/La values typically correlated with increasing fluids from the slab.

The influence of melt structure on the partitioning of trace elements

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Partitioning of trace elements between melt and crystal is a versatile tool to reconstruct the origin of igneous rocks, thus it is essential to understand the controlling parameters. It is generally accepted that the partitioning of trace elements (TE) is controlled by T, p, fO2 and crystal chemistry (e.g. [1]). Several studies have also proposed a significant influence of the melt composition and thus melt structure on TE partitioning [2–4]. Particularly, Prowatke & Klemme’s results [4] on TE partitioning between melt and titanite, which varied over several orders of magnitude, suggest a strong control of the melt composition and thus melt structure. To date there is no clear understanding of the relationship between melt structure and element partitioning. Ponader & Brown [5] report already that coordination of some rare earth elements (REE) in quenched melts changes with the degree of polymerization of the melts, this was used to explain differences in chemical partitioning. However they did not provide a direct correlation between the analysis of the element coordination and partitioning data.

In this study, different melt compositions were taken from Prowatke & Klemme [4], doped with selected REE (0.5 wt%, 2 wt%) and synthesized as glasses. EXAFS was used to get information about coordination and radial distances to the neighboring atoms of the REE in the glasses. Resonant Inelastic X-ray Scattering (RIXS) provides information about the electronic structure and was used to derive further constraints on the coordination. The measured EXAFS spectra show small variation in the distance to the first oxygen neighbors to the different glasses. The RIXS and high resolution XANES indicate only slight differences in site symmetries. Although only preliminary, our results show that the strong difference in element partitioning correlates only with rather small changes in the TE coordination.


Formation of carbonate minerals during magmatic/hydrothermal alteration of volcanic rocks at Unzen volcano, Japan

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The alteration processes of dacidic and andesitic rocks of Unzen volcano are characterized by almost complete substitution of amphibole phenocrysts with two types of carbonates (up to 20 wt. %), quartz, muscovite and chloride. In this study we investigate the main factors responsible for the alteration of porous volcanic rocks at Unzen.

It is determined that unaltered dacite has pores in the range from 100 nm to 10 µm, whereas the most frequent pore sizes for coherent altered dacites are observed in the range between 30 and 400 nm. All samples are characterized by interconnected porosity.

The unaltered amphiboles exhibit a homogeneous oxygen isotopic composition, with δ18O vs VSMOW varying between 6.6 and 7.0‰, pointing to their primary magmatic origin. The oxygen isotopic composition of carbonates substituted amphiboles ranges from 6.0 to 9.1‰ vs VSMOW and their carbon isotopic composition varies between –4.7 and –6.4‰ vs VPDB. It implies that magmatic CO2 and primary silicates provide the main sources for the carbonate carbon and carbonate oxygen, respectively. Hydrogen isotope composition of unaltered amphiboles shows typical magmatic signatures (δD=–48‰) without any evidence for late- or post-magmatic contamination by meteoric waters.

A series of hydrothermal fluid/rock interaction experiments in different systems, i.e. dacidic or pure amphibole + H2O, H2C2O4, Ag2C2O4, Pl, CaCO3 in different proportions were conducted at temperatures from 300 to 700°C and at pressures from 100 to 300 MPa, respectively. The first analyses of the experimental products show that amphiboles participate in exchange reactions with fluid with the formation of new mineral phases, e.g. CaSiO3, however the size of produced phases was too small for proper identification. Raman spectra confirm that carbonates are indeed present as secondary phases in altered amphiboles (<5µm), providing constraints on the carbonate reactions.

Further experiments are required to reproduce natural mineral assemblages and to determine typical conditions for carbonate formation in Unzen conduit.
Do $^{226}\text{Ra}-^{230}\text{Th}$ isochrons provide realistic crystallization ages?

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In this contribution we investigate the timescales of magma genesis, melt evolution, crystal growth rates and magma degassing in the Mt Erebus magmatic system using measurements of $^{238}\text{U}-^{230}\text{Th}-^{226}\text{Ra}-^{210}\text{Pb}-^{210}\text{Po}$; $^{232}\text{Th}-^{228}\text{Ra}$-degassing in the Mt Erebus magmatic system using genesis, melt evolution, crystal growth rates and magma and $^{230}\text{Th}-^{226}\text{Ra}$ are significant and uniform over the 36 year years 1984, 1989, 1993, 2004, 2005. These samples $^{238}\text{U}-^{230}\text{Th}$ anorthoclase megacrysts separated from historic bombs for the consists of 22 historic bombs, ranging from 1972-2005; and 5 decay series nuclides in a volcanic system. Our sample suite set to present the entire suite of relevant $^{238}\text{U}$, $^{235}\text{U}$ and $^{232}\text{Th}$ phonolite glass $^{228}\text{Ra}/^{232}\text{Th}$ is in equilibrium, whereas in the systematics. However, the significant $^{228}\text{Ra}/^{232}\text{Th}$ disequilibria. More importantly, this model shows that when the timescale of crystallization is comparable to the half-life of $^{226}\text{Ra}$, the simple $^{230}\text{Th}-^{226}\text{Ra}$ isochron techniques typically used in most U-series studies likely provide erroneous ages.

Dissolved $^{230}\text{Th}-^{232}\text{Th}$ dynamics in the Eastern Tropical Pacific Ocean

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We present data for dissolved $^{230}\text{Th}$ and $^{230}\text{Th}$ concentrations in seawater from nine depth profiles along a transect (~85°W) from about 7°N to 8°S in the eastern tropical Pacific Ocean. Our sampling sites cover the highly productive regions of the Pacific cold tongue close to the equator, and less productive regions of the Panama and Peru Basins. Dissolved $^{230}\text{Th}$ is thought to be scavenged onto sinking particles, and reversible exchange between dissolved and particulate phases takes place throughout the water column. As a result vertical dissolved $^{230}\text{Th}$ profiles should show a linear increase in $^{230}\text{Th}$ concentration with increasing water column depth.

Filtered (dissolved fraction of $^{230}\text{Th}$-$^{232}\text{Th}$) and unfiltered (dissolved and particulate fraction of $^{230}\text{Th}$-$^{232}\text{Th}$) seawater samples have been processed following established protocols developed by GEOTRACES. Our data thus far show little evidence for a linear increase in the concentration of dissolved $^{230}\text{Th}$ with depth, and the observed vertical structure may be related to either water mass or particle flux effects. Dissolved $^{230}\text{Th}$ concentrations range from 0.25 to 1.46 dpm/1000L for filtered samples. Dissolved $^{230}\text{Th}$ concentrations are low and range from 0.002 to 0.007 dpm/1000 L for filtered samples. While concentrations of $^{230}\text{Th}$ are slightly higher in the unfiltered samples, $^{230}\text{Th}$ concentrations are usually much higher in the unfiltered samples (up to 170% higher), compared to those concentrations in the filtered samples. The greatest differences between filtered and unfiltered Th concentrations occur in the bottommost samples. Our preliminary results also indicate that there is a concentration gradient along the transect—higher concentrations of $^{230}\text{Th}$ are found in the low-particle-flux Peru Basin while very low concentrations of $^{230}\text{Th}$ have been determined in profiles closer to the Panama Basin. Like the $^{230}\text{Th}$ data, the $^{232}\text{Th}$ concentrations are highest the further south in the transect. However, in contrast to the $^{230}\text{Th}$ concentrations, there is little structure in the $^{232}\text{Th}$ concentrations, which vary little with depth.
Grain size analysis of sediments of Thar Desert, India to infer sedimentary environment

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Grain size is a fundamental descriptive measure of sediment and sedimentary rock. Grain size parameters are useful for recognizing sedimentary environments as dune, river, beach marine and others of continental shelf through graphical, moment and statistical methods. Bivariate plots between various statistical grain size parameters can be successfully used for distinction of such environments. The statistical grain size parameters were treated using different statistical tools such as factor and discriminatory analysis to decipher the depositional history of the sediments of the study region. The analysis suggests that the deposits are not unequivocally aeolian, but contain sediments contributed by marine, shallow marine, fluvial, aeolian and lacustrine processes. Fluvial and fluvo-lacustrine deposits formed the base for the aeolian deposition in the region. SEM analysis of grains are a type of caliche formation in which fine grained calcareous sediments has reached near surface by capillary action and deposited. Angular outlines and features such as high relief, sharp edges and articulate steps were observed in the grains. The results of bivariate plots of mean (phi), moment mean and discriminant analysis does not show any specific trend of grain size for different geomorphic environments however these functions states that the sedimentary depositional environment in the study area has been mainly controlled by fluvial and marine activities but the importance of aeolian action also can not be ignored.

Geochemistry and mineralogy of Tertiary sedimentary rocks from Kerala, South India – Implications to REE behaviour under intense chemical weathering

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The Tertiary sedimentary rocks of Kerala along the south-west coast of India are mainly divided into three formations, Vaikom, Warkala and Quilon. This research evaluates the clay mineral and geochemical compositions including the rare earth elements (REE) of the mudstones and sandstones from two sedimentary sections of Warkala formation from the Karuchal and the Warkala region. The high CIA values ranging between 97 and 99 for Karuchal area and between 85 and 98 for Warkala area suggests that these sediments are extremely weathered. Further Kaolinite as the dominant clay in rocks from Karuchal section and Kaolinite / Gibbsite as the dominant clay in rocks from Warkala section also corroborate higher degree of weathering. All elements except Al, Ti and Ni exhibit depletion in comparison to UCC. The chondrite normalised REE pattern exhibit high degree of fractionation, ((Ce/Yb)n ranging between 30 and 67 for sediments of Karuchal section; (Ce/Yb)n ranging between 14 and 50 for sediments of Warkala section. On normalizing with all the probable source rocks exposed in the area, the REE plot of the sediments exhibit LREE enrichment and HREE depletion. This indicates that the higher (Ce/Yb)n ratios are not because of source, but due to the loss of HREE and residual enrichment of LREE bearing phases. This suggests mobilisation and removal of HREE from the system under extreme chemical weathering. Our finding has important implications as REE is commonly accepted to reflect the nature of exposed continental crust [1].

**Sustainable water resource management in Eastern Punjab using remote sensing and GIS to demarcate water potential zones**

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Water is a fluctuating resource making it difficult to measure in time and in space. To demonstrate the efficiency of the geographic information system (GIS) for groundwater management, information on the parameters controlling groundwater such as lithology, geomorphology, soil type, land use and land cover and lineament analysis were analyzed. IRS LISS-III and Landsat satellite data of the area was used to infer information on the geologic lineaments and geomorphology. To identify linear features i.e. lineament enhancement and directional filtering was performed on single bands of Landsat images. Thematic maps for geology, slope, soil, geomorphology and lineament were prepared and integrated in GIS by assigning the weights and ranking to various parameters controlling the occurrence of groundwater to generate the groundwater potential map for the study area. The results indicate that the floodplain of river and its adjoining areas have very good groundwater potential, whereas the steeply sloping area in the northern part having high relief and slope possesses poor groundwater potential. The groundwater potential zones were obtained by weighted overlay method using the spatial analysis module in ArcGIS 9.0. The southern part of the study area showed highest decline in water level in last 3 decades. Thus a holistic water resource management strategy needs to be developed for this part of the district. The floodplain of the river in the area holds potential for further groundwater development as these areas belong to good class in GPI map.

**Toward a self-consistent pressure scale: Elastic moduli and equation of state of MgO and Ringwoodite by simultaneous X-ray density and Brillouin sound velocity measurements at high-P and high-T**

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Accurate phase diagrams and PVT equations of state (EOS) of materials strongly depend on the PVT calibrations of standard materials (e.g. MgO, NaCl, Au, Pt), which currently do not predict identical pressures at the same experimental conditions. MgO is one of the simplest and most studied materials and is a common pressure standard, although its accurate high-PT EOS is still uncertain. The direct way of obtaining a self-consistent pressure scale is by measuring acoustic velocities (Vp and Vs) and density simultaneously. Such P-V-T-Vp-Vs measurements allow one to determine the pressure directly, without resort to a separate calibration standard.

Recently, as part of a major COMPRES initiative, we have constructed a Brillouin spectrometer at GSECARS, APS, which allows accurate simultaneous sound velocity and lattice parameter measurements at high P and high T. Such measurements were performed on single crystal MgO in diamond cells. At each PT we measured the unit cell parameters and the acoustic velocities in several crystallographic directions, and directly obtained all three single crystal, and isotropic adiabatic bulk (Ks) and shear (μ) elastic moduli.

In addition we demonstrate that successful P-V-T-Vp-Vs measurements can be performed on certain polycrystalline materials, e.g. Ringwoodite (gamma-Mg₂SiO₄). The results of these experiments and implications for a self consistent P-V-T (-Vp-Vs) pressure scale will be presented and discussed.
**In situ** Fe-Mg isotopic analysis of zoned olivines

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Chemical diffusion profiles in zoned olivines may be used to infer the thermal history of the system surrounding them. However, diffusive transport is not the only way to produce a chemical gradient. An olive that crystallized rapidly may produce a similar zoning pattern.

Fe and Mg isotopic analyses of bulk olivines reveal that isotopes can be used to recognize chemical diffusion in olivines [1-3]. Chemical diffusion can induce large isotopic fractionations because light isotopes always diffuse faster than their heavier counterparts [4-5]. At equilibrium, little isotopic fractionation is expected given the high temperatures of magmatic systems.

Olivines in Kilauea Iki lava lake have large chemical zoning profiles and lighter iron isotopic compositions than the bulk basalts [1]. Teng et al. [1] showed that in these olivines, the isotopic compositions are correlated by a slope of -3.3 in a plot of δ56/54Fe vs. δ26/24Mg, in close agreement to the predicted slope of -2.7 for binary diffusion [2]. Here we provide definite evidence that diffusive transport is responsible for the light Fe isotopic compositions measured in olivines in Kilauea Iki lava lake.

A zoned olivine ~4 mm in size was microdrilled in two orthogonal traverses for Fe and Mg isotopic measurements. Isotopic compositions were measured by MC-ICPMS. Profiles are observed with iron isotopic compositions ranging from -1.2 ‰ in the core to -0.2 ‰ in the rim (δ56/54Fe deviations from IRMM-014). The variations can be explained by diffusion of Fe into olivine following magmatic evolution towards more Fe-rich and Mg-poor compositions.

**Potentially toxic metal bearing mineral phases in total suspended particles from Budapest, Hungary**

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Total suspended particles (TSP) in the urban air can be both inhaled and ingested so causing health damage due to their size, shape or toxic components. In this study mineralogical (XRD, AEM), geochemical (XRF) and magnetic (MS) analyses were performed to characterize the mineral phases containing potentially toxic metals in TSP from three sampling sites in Budapest. The samples represent a wide range of physico-chemical properties. Their particles are generally below 50 μm with a maximum frequency at around 10-12 μm. Between 45 and 80% of their particles belong to the PM10 fraction. They show significant enrichment in several potentially toxic metals with concentrations 1342-19 046 mg/kg for Zn, 434-3597 mg/kg for Pb, 394-699 mg/kg for Zn and 38-144 mg/kg for As. Their main mineral components reflect the geological characteristics of the sampling areas. Additionally, large amount of magentite (up to 15%) and amorphous organic matter, as well as gypsum and halite was also found in the samples.

The most important toxic metal bearing mineral phases are spherulitic or xenomorphic magnetite particles containing 2-3 wt% Pb and Zn. These magnetite particles often form aggregates and are closely associated with soot and/or clay minerals. In samples with high magenetite content toxic metal-free magnetite spherules up to a few micrometer size also appear. The magnetic analyses showed that the sizes of the magnetite particles is rarely below 30 nm. Clay minerals and mica particles may also contain significant amount of Zn (up to 5wt%). Additionally, ZnO and ZnCO₃ particles were also found in the sample with highest Zn content. Magnetite particles are resistant to weathering releasing its toxic components slowly to the environment, while layer silicates may be the source of mobile toxic metals in these samples. The study was financially supported by the OTKA (K 76317 and K 75395).

Pyroxene and olivine exsolution textures in majoritic garnets from the Mir kimberlitic pipe (Yakutia)


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Majoritic garnets are widely abundant as inclusions in diamonds worldwide [1]. Pyroxene exsolution textures were registered in garnets from mantle xenoliths in kimberlites [2, 3], as well as in rocks of ultrahigh-pressure metamorphic complexes [4], which provides evidence for their crystallization at pressures >7–8 GPa. We studied three large (>5 mm) garnet xenocrysts (Samples 317, 559 and 563) from the Mir pipe (Yakutia) containing regularly oriented pyroxene and olivine lamellae with angles of 71°–72° between them. Garnets of all samples are pyrope-rich (75.1–78.6 mol %), with medium CaO (4.5–5.8 wt %) and low Cr2O3 (up to 0.59 wt %) concentrations. Clinopyroxene lamellae are enriched in diopside component (89.9–94.4 mol %). Olivines are characterized by the high Mg# (up to 0.96) and extremely high NiO concentration (1.6 wt % in Sample 559; 2.79 wt % in Sample 317). According to the data of 3D X-ray tomography using a scanner SkyScan1172 and 3D analysis (CT-An software), garnet (Sample 317) contains 9 vol % pyroxene and 0.5 vol % olivine lamellae. Calculation of the compositions of primary garnets demonstrated that Si content in them exceeded 3 f.u. (3.084 in Sample 559; 3.088 in Sample 563; 3.094 in Sample 563) providing evidence for incorporation of majoritic component. The formation of such garnets occurred at pressures >7.5 GPa and high temperatures (Ni in majoritic garnet and olivine). Subsequent decrease of PT parameters to 3.0–3.1 GPa and 950–1000°C [5] resulted in pyroxene and Ni-olivine exsolution in former majoritic garnet.

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Effects of organic ligands and temperature on the kinetics and mechanisms of olivine carbonation

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The slow dissolution kinetics of Mg-rich silicates has become a critical issue for the geologic CO2 sequestration in basic rocks. Previous batch carbonation studies on San Carlos olivine performed in CO2 saturated water (at 90°C and PCO2=280 bar) have focused on the role that secondary phases, such as amorphous silica layers (SiO2 (am)), have on the transport of reactants from and to the reactive surfaces. The fluid composition remained roughly constant over the duration of the experiment, close to saturation with respect to amorphous silica and with a [Mg2+]/[SiO2 (aq)] ratio close to stoechiometric release, suggesting a passivation of the olivine surface by the silica layer.

In order to accelerate the dissolution process, organic ligands such as citrate and acetate were added to the solutions and tested at 1M and 0.1M concentrations in similar batch experiments. An intrinsic increase of the dissolution rate of olivine was expected prior to the formation of a passivating silica layer.

Preliminary results confirm this idea since Mg was released in non-stoechiometric proportions with respect to SiO2 (aq) (found to be in equilibrium with SiO2 (am)). Similarly, a slight increase of temperature (from 90°C to 120°C) accelerated the reaction kinetics as well, possibly impacting the textural properties of SiO2 (am). Current TEM investigations are directed to confirming a possible link between the observed increase of the rate and textural properties of secondary phases. In addition, because carbonate minerals have a retrograde solubility, thermodynamical modelling suggests that this temperature increase should allow the fluid to reach saturation with respect to carbonates before reaching saturation with respect to SiO2 (am). Enough Mg can therefore be released to initiate the formation of carbonates before the silica precipitates and passivates the olivine surface.
Impact of the earthworm *Lumbricus terrestris* on arsenic mobility and speciation in soil

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Earthworms can be found living in arsenic contaminated soil. Generally earthworm activity increases the mobility and bioavailability of contaminants [1]. Using soil collected from Devon Great Consols containing 1150 mg As kg⁻¹ we have investigated how the secretion of earthworm mucus and the passage of soil through the earthworm gut impacts mobility and speciation of As.

*Lumbricus terrestris* were cultivated in the As-contaminated soil and the casts collected. Water soluble As increased from 1.6 mg kg⁻¹ in the bulk soil to 18 mg kg⁻¹ in the casts. Casts were then aged and this effect was still present 56 days after soil excretion. Analysis indicated that these changes were due to release of As(V) from soil particles during the digestion process as a result of increases in pH and increased concentrations of dissolved organic carbon. No reduction of As(V) to As(III) was detected despite passage of the As through the anoxic rear-gut of the earthworm.

Solutions of earthworm mucus were produced by washing earthworms with deionised water. These solutions were then used as an extractant for the As-contaminated soil. At low mucus concentrations As extraction was reduced relative to deionised water due to formation of ternary complexes between the amino acids present in the mucus, As and surfaces of Fe oxyhydroxides. However, at higher mucus concentrations increased pH and dissolved organic carbon effects dominated resulting in increased extraction of As.

The mobilisation of As (and other elements) from contaminated soils in the environment by cast production and mucus secretion may allow for accelerated leaching or uptake into biota which is under-estimated in current risk assessments based on analysis using soils in the absence of soil biota.


Continental subduction, slab breakoff and eduction: End-member processes for UHP rock histories

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We conducted a set of numerical experiments to study the evolution of a subduction–collision system subject to spontaneous slab breakoff. The study takes into account complex rheological behaviour including plasticity, viscous creep and Peierls creep and mineralogical phase transformations including UHP melting. A limited number of contrasting geodynamic scenarios were observed that combine several previously suggested end-member tectonic processes such as continental subduction, multiple crustal stacking, oceanic slab delamination and breakoff, plate eduction, ductile crustal extrusions and buoyant partially molten trans-lithospheric plumes. In the explored parameter space, breakoff depth can range from 40 to 400 km with Peierls creep in the cold subducted mantle been a key mechanism for slab necking. We also found that melting of crustal materials at ultrahigh pressure metamorphic (UHPM) conditions can trigger the exhumation of high temperature-ultrahigh pressure metamorphic (HT-UHPM) rocks. In the model, the generation of temperatures high enough for anatexis during subduction is due to the continental crust and associated sediments coming into contact with hot asthenospheric mantle of the wedge at ultrahigh pressure conditions. The consequent enhanced buoyancy of the melt-bearing crustal and associated sedimentary materials drives the subsequent exhumation of the HT-UHPM rocks from mantle depths to mid- to-lower crustal levels. Exhumation occurs by a thermally induced slab-parallel ductile extrusion of melt-bearing crustal materials along the interface between the stagnant subducted slab and the mantle wedge. The up to 1000 C peak temperatures achieved in the experiments at UHPM conditions are the highest obtained so far in experiments using numerical models; they are similar to many natural HT-UHPM rocks. The sensitivity studies suggest that some other mechanisms proposed previously for the exhumation of UHPM rocks including multiple crustal stacking, plate eduction, trans-lithospheric crustal plumes and channel flow are mainly controlled by the oceanic slab age and length and by the incoming passive margin geometry. Indeed, all these exhumation processes typically result in colder P-T paths with the coldest (<500 C) peak temperatures been produced by the eduction-driven exhumation.
Trace elements and lead isotopes in moldavites: Source material fractionation or variable parent lithologies mixing?

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Samples and data collection

Contents of selected minor and trace elements and lead isotope composition have been determined for 16 moldavites from South Bohemian (4), West Moravian (5) and Cheb Basin (7) partial strewn fields. Data were measured using ICP-MS technique from solution following the protocol of Strnad et al. [1].

Results

After normalizing the measured values to average element contents for moldavites from the South Bohemian partial field it appeared that the moldavites from Cheb Basin differ from those from South Bohemia and Moravia. They are highly enriched in Zn, Ba, Pb, and U while they display significant depletion in Cr and Ni. Moravian moldavites display either no or significantly less differences when compared to South Bohemian moldavites.

Chondrite-normalized REE contents overlap existing literature data. HREE tend to be enriched in Moravian samples whereas the samples from the Cheb Basin appear to be depleted in HREE compared to the moldavites from the South Bohemian field. Concentrations of LREE remain more or less invariant among all regions.

In the plot \( \frac{^{208\text{Pb}}}{^{206\text{Pb}}} \) vs. \( \frac{^{206\text{Pb}}}{^{207\text{Pb}}} \) the moldavites from the Cheb Basin are clearly separated from the rest of the samples analyzed; samples from South Bohemia and Moravia do not differ.

Conclusions

The data collected do not corroborate idea of selective source material fractional vaporization, or that of selective condensation neither the hypothesis of Engelhardt et al. [2] explaining the formation of moldavites by preferential trapping of large ions into early condensates. We assume that measured composition reflects the lithological variability of the target area instead.


Nitrogen isotope fractionation during the oxidation of substituted anilines by manganese oxide

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Primary aromatic amino groups are often the position of initial attack during the mineral-catalyzed oxidative transformation processes of soil and groundwater contaminants. Here, we explored the N isotope fractionation associated with the oxidation of substituted anilines as a diagnostic tool for identifying the initial oxidation steps of such degradation processes. Apparent \(^{15}\text{N}-\text{kinetic isotope effects}, \text{AKIE}^{\text{N}}\), were determined for oxidation of various substituted anilines in suspension of manganese oxide (MnO\(_2\)) and compared to reference oxidation experiments in homogeneous solution and at electrode surfaces, as well as to density functional theory calculations of intrinsic KIE\(_{\text{N}}\) for electron and hydrogen atom transfer reactions.

Spectroscopic characterization of MnO\(_2\)-particles as well as the investigation of co-solute effects on mineral reactivity showed that despite complex reaction kinetics of contaminant disappearance, substituted aniline oxidation occurred in one elementary, isotope-sensitive reaction step. Owing to the partial aromatic imine formation after one-electron oxidation and corresponding increase in C–N bond strength, AKIE\(_{\text{N}}\)-values were inverse, substituent-dependent, and confined to the range between 0.992 and 0.999 in agreement with theory. However, AKIE\(_{\text{N}}\)-values became normal once the fraction of cationic species prevailed owing to \(^{15}\text{N}-\text{equilibrium isotope effects}, \text{EIEN}\) of 1.02 associated with N atom deprotonation. The observable AKIE\(_{\text{N}}\)-values are substantially modulated by the acid/base pre-equilibria of the substituted anilines and isotope fractionation may even vanish under conditions where normal EIEN and inverse AKIE\(_{\text{N}}\) cancel each other out. Our work suggests that the observed pH- and substituent-dependent trends of N isotope fractionation provide a new line of evidence for the identification of oxidative degradation processes of substituted primary aromatic amines.
Solubility and toxicity of hydroxylapatite (hap) nanoparticles (nps): Implications for nanobiomaterial safety
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Nanotechnology has the potential to solve many of modern society's problems, notably in medicine and the environment. Although an increase in interest in regulating risks from nanotechnologies is evident in recent years, research and regulation of risks lag behind the driving forces of intellectual curiosity and commercial potential. The aim of this work is to contribute to a better understanding of the risks of nanotechnology and ultimately to their control. We specifically focus on the reactivity and the potential toxicity of HAP NPs, which are used in many medical innovations.

A variety of HAP NPs were synthesised selected on the basis of their biocompatibility and particle size. Full detailed physicochemical characterisation was carried out in parallel. The synthesis method was then optimised to provide control over crystal growth, agglomeration, particle size and shape mainly by investigating the effect of synthesis parameters such as: synthesis temperature, pH, maturation time, concentration of the capping agent, drying and calcination temperature.

The reactivity/chemical stability of the nanoHAPs was assessed by solubility experiments, which showed that solubility exponentially increases as the grain size decreases. This is in agreement with the modified version of the Kelvin equation, which describes the prediction that solubility is dependent on the particle size and is expected to increase exponentially as particles get smaller. Furthermore, these experiments showed that solubility correlates well with the crystallinity of nanoHAPs.

Protein adsorption studies were carried out as a proxy for toxicity; high proportion of protein adsorbed indicates better biocompatibility, and therefore less likelihood for toxicity. These experiments showed that more protein was absorbed by the smallest, least crystallised and non-functionalised HAP NPs, suggesting that these are the most biocompatible nanoHAPs.

Flux rates for water and carbon during greenschist facies metamorphism
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The time-averaged flux rate for a CO2-bearing hydrous fluid during greenschist facies regional metamorphism was estimated to $10^{10.2} \pm 0.4$ m$^3$. m$^{-2}$. s$^{-1}$. This was evaluated by combining 1) Peclet numbers obtained by chromatographic analysis of the propagation of reaction fronts in 33 metamorphosed basaltic sills in the SW Scottish Highlands (Fig. 1), 2) empirical diffusion rates for CO2 in water obtained by Wark & Watson (2003), and 3) calculated time-averaged metamorphic porosities. The latter were calculated using an expression obtained by combining estimated Peclet numbers with the empirical porosity – permeability relationships obtained by Wark and Watson (1998) and Price et al. (2006) and Darcy’s law. This approach yielded a time-averaged metamorphic porosity of $10^{1.5} \pm 0.2$ for greenschist facies conditions. The corresponding timescale for metamorphic fluid flow was $10^{3.6} \pm 0.1$ years. By using mineral assemblages to constrain fluid compositions, I further obtained a time-averaged annual flux rate for carbon of 0.5-7 mol-C. m$^{-2}$. yr$^{-1}$. This matches measured emission rates for metamorphic CO2 from orogenic hot springs. These fluxes significantly exceed estimated rates of CO2 drawdown by orogenic silicate weathering and therefore indicate that orogenesis is a source rather than a sink of atmospheric CO2.

Figure 1: Photomicrograph (in XPL) showing replacement of amphibole by calcite: evidence of carbon transfer, preserved in a metabasaltic sill from the SW Scottish Highlands.
Tracing episodic magma accretion by zircon $^{18}\text{O}/^{16}\text{O}$ isotopes and U-Pb dating in the Adamello batholith, Italy

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Styles and timescales of batholith formation still remain a matter of debate. There is growing evidence that batholiths are not formed by a single ascent of magma but by accretion of multiple batches. In the latter case, are they derived from the same source or different ones, and do they suffer similar degrees of contamination?

In order to answer these questions, we study tonalites from the Adamello batholith (33-43 Ma) localized in the northern Italian Alps. Previous studies mainly based on cooling ages highlighted a younging of magmatic activity towards the north [1, 2, 3], which is confirmed by our new U-Pb zircon LA-ICP-MS dating. Isotopic compositions of both Sr and O indicated increased contribution from higher $^{18}\text{O}$, more radiogenic supracrustal sources in the same direction [4]. We present new data from a $^{18}\text{O}/^{16}\text{O}$ isotope study on small quantities of freshest and refractory separates of quartz, amphibole, titanite and zircon, and best estimate $^{18}\text{O}$ magma values [5]. The data confirm increasing crustal contamination towards the north indicated by elevated $^{18}\text{O}$ values up to 7‰ in zircon. H isotope ratio is strongly negative (-97‰) for the amphibole in the most northerly sample suggesting an assimilation of hydrothermally-altered rocks or an assimilation of marine sediment. We will quantify the contamination by AFC modelling using geochemistry, whole rock and mineral isotopes. As a preliminary conclusion, the Adamello batholith was formed by different pulses over ca 10 m.y. coming from different in $^{18}\text{O}$ magma reservoirs with contrasting oxygen isotope compositions, due to their different depth in a $^{18}\text{O}/^{16}\text{O}$ zoned crust.

The 1.86-1.84 Ga magmatism in the Western East European Craton (Lithuania): Implications for a convergent continental margin

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The East European Craton in western Fennoscandia was mostly formed by the accretion of distinct terranes at c. 1.8 Ga. TTG magmatic rocks in the age range 1.86-1.84 Ga are abundant in the crystalline crust of S, central and NW Lithuania. In the south, TTG rocks compose the large Randamonys massif. A Zm347 tonalite yielded an 1859±5 Ma concordia age, while a Vr268 diorite was dated at 1848±6 Ma. A strongly deformed 7Gr granitic rock in adjacent NW Belarus gave a similar 1844±8 Ma igneous age. In central Lithuania, the Glv99 igneous mafic granulites display magmatic 1839±15 Ma and metamorphic 1809±9 Ma ages. The nearby Grz105 gneissic granite was intruded at c. 1837±6 Ma, while the Kz65 granite further north was emplaced at 1844±5 Ma [1]. The area to the south and west of the above described rocks in Lithuania and in N Poland is dominated by younger c. 1.83-1.79 Ga magmatic rocks. The fragments of a c. 1.83-1.82 Ga volcanic island arc in Sweden [2], N Poland and Lithuania [3] compose a considerable part of this younger domain.

The distribution of 1.86-1.84 Ga magmatic arc-related rocks in Lithuania likely delineates fragments of a convergent continental margin. It continues northwards across the Baltic Sea into south-central Sweden, and southwards to N Poland and NW Belarus.


Abnormal (Y+REE)-enriched zircon from the pegmatite dike (Gridino, the Belomorian province, Fennoscandian shield)

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Zircon can contain naturally U and Th up to 10 wt% and several thousands of ppm of REE. The maximum known contents of REE (up to 98, 154 ppm) was found in zircons from Bidoudouma stream close to Oklo, Gabon [1].

We found abnormal (Y+REE)-enriched zircon in the thin pegmatite dike cutting precambrian eclogites (village Gridino, the Belomorian province, Fennoscandian shield, see outcrop photo in [2]). Zircon core (207Pb/206Pb-age 2685 Ma) is captured eclogite protolith with regular REE distribution. Rim is characterized by high contents of REE (61, 280–96, 760 ppm), Y (55, 360–84, 800 ppm) and distinctly positive Ce anomaly. U and Th contents are not so high – maximum 2230 and 90 ppm, respectively.

Age of rim crystallization is svecofennian (1875 Ma) following high-pressure metamorphism event

Figure 1: REE patterns for zircon core and rim (insert is CL image)

Nanoparticle bioremediation: Application of solid phase capture

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The use of engineered nanoparticles continues to expand rapidly. As this intensifies, so does the environmental risk posed if they are released into the environment. This is of particular concern due to the potential toxicity of some nanoparticles. As it stands, we are poorly prepared to deal with nanoparticle pollution and thus remediation strategies must be developed. Here ureolysis-driven calcium carbonate precipitation by the urease positive bacterium Sporosarcina pasteurii is investigated as a means of removing nanoparticles from aquatic systems. This technology has been investigated for the solid phase capture of radionuclide and trace element contaminants in groundwater systems [1]. However its potential to capture nanoparticles has yet to be examined.

Batch experiments showed the successful removal of highly stable organo-metallic nanoparticles at concentrations up to 10mg/l (the highest concentration tested thus far). Over 90% of nanoparticles were captured within 24 hours and capture efficiency appeared to be inversely proportional to calcite precipitation rate. As calcite precipitated, the nanoparticles became trapped within the growing calcite crystal. As the calcite-nanoparticle composite continued to grow, it adhered to surfaces (such as the edge of the reaction flask, or the edge of a pore space), immobilizing the nanoparticles from solution. Nanoparticles are believed to act as nucleation sites for the precipitating calcite. First order reaction kinetics were calculated to determine reaction rate constants, and in particular, $S_{cr}$, the critical saturation required for nucleation. This technology has the potential for application in contaminated groundwaters and soils as an in situ remediation technique for nanoparticle pollutants.


Testing a geochemical tracer tool in New Zealand water

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Deteriorating water quality along the Tarawera River, in Kawerau (New Zealand), is thought to be correlated to the solid and liquid waste disposal practices of the local pulp and paper mill in conjunction with naturally occurring geothermal discharge in the area. Due to high concentrations of boron in the liquid from both of these sources this study investigates the use of this element as a tool to assist in improving the management of the waterways and water quality in the region.

Comprehensive scientific studies that have been conducted for over 20 years have identified boron as a successful natural tracer for use in water bodies in different parts of the world. [1-3] Drawing on this information we executed a temporal water quality survey to assess the consistency of boron isotope composition values at a localised scale. This survey included monthly sampling over a six-month period spanning the wet and dry seasons. The water samples were a selection of pond, river, ground (shallow and deep zones), and geothermal, coupled with leachate and aeration pond water from a pulp and paper solid waste site. The boron concentration data and isotope ratios were established using ICP-MS and negative TIMS, respectively.

This paper discusses: 1) the effectiveness of boron isotope composition values as signatures for water; 2) the reliability of these signatures as a tool for water quality and management purposes; 3) the level to which sampling, analytical and environmental anomalies have influenced the results.

Factors affecting detrital zircon age distribution – Natural samples and experimental approach

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We have investigated some of the factors that affect the accuracy of detrital zircon age provenance studies. The main goal was to quantify the effects of individual factors in the deviation of the measured detrital age spectra from the real zircon age distribution in the sediment and in the sediment source. The analysis has been carried out in a natural catchment in the Scottish Highlands representing simple two-component source system and on samples of synthetic sediment prepared on purpose for this study using zircon-free quartz sand and known number of zircon grains of known age distribution. Our results suggest that the zircon fertility of the source rocks and physical parameters of zircon grains represent the most important factors affecting the distribution of zircon age populations in the stream sediments. It can account for a several-fold difference between the ratio of the rocks in the source area and abundance of zircon in the sediment. Additional age biases can be introduced during sample preparation and data processing. The sample preparation and selection of zircons from the mineral concentrate may result in preferential loss of small grains and enhancement of the age component represented by larger grains. This can, together with the preference for larger grains during handpicking, cause several-fold difference compared to the real age distribution in the sediment sample. These factors appear to be more important for the reproducibility of zircon age spectra than is the number of zircon grains analyzed per sample. Even the most abundant age population in the sample may deviate by tens of percent from its real content in the sediment after hundred or more analyses have been done. The complex relations between proportion of zircon age populations in the source, sediment and analyzed sample make it difficult to relate the peak intensity in the age spectra to the sediment quantity contributed from different sources. At all times, the analytical limits of the dating techniques must be considered when evaluating potential overlap of zircon populations that are closely spaced in time. Although the visualization of U-Pb data in probability density plots is commonly used for comparison between samples, the detrital zircon age spectra must always be interpreted relative to the volume of individual age populations, not to the intensities of the age peaks.

Fluoride removal by calcite – Stirring rate/temperature effects

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Fluoride contamination of groundwater due to anthropogenic activities remains a major concern for many industries worldwide. The effects of stirring rate and temperature on the removal of fluoride by calcite have been studied in order to determine the most efficient and cost effective method of remediating such contamination. The kinetics of calcite dissolution and precipitation in aqueous solution has been the subject of numerous investigations. However, little study has been undertaken on heterogeneous systems where mass transport processes and surface reactions determine rates. Aleksey, et al. [1] have noted that traditional thermodynamic approaches to determine equilibrium are problematic and there is a need for a kinetic approach to solving these problems. The effects of stirring and temperature on the heterogeneous calcite/F systems are the focus of this study.

A series of free drift experiments were conducted in a controlled temperature (CT) room at 20°C, 30°C and 40°C, with P CO2 in equilibrium with the atmosphere (P CO2 = 10−3.5). Calcite was added to potassium fluoride solutions and stirred at 0, 200 and 300rpm using an overhead stirrer. The results in Table 1 have been determined by fitting the experimental data to the non-linear Hill 1 function (r2 >0.98).

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</table>

Table 1: Time (min) to reach equilibrium F removal

The results clearly demonstrate that a greater rate (dF/dt) of fluoride removal is possible with increased stirring rate and temperature. Early in the reaction <200 minutes dissolution is largely a function of a surface reaction as mixing has little effect on the rate [2]. In the latter part of the reaction, stirring rate has a significant effect, consequently hydrodynamic transport effects dominate [2].

Minerals of $\text{Pt}_3\text{Sn-Pd}_3\text{Sn-Pd}_3\text{Pb-Pd}_3\text{As-Pd}_3\text{Sb}$ system in PGE-Cu-Ni and PGE ores of the Norilsk region

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All minerals of the system – rustenburgite $\text{Pt}_3\text{Sn}$, atokite $\text{Pd}_3\text{Sn}$, zvyagintsevite $\text{Pd}_3\text{Pb}$, guanglinite $\text{Pt}_3\text{As}$ and unnamed mineral with $\text{Pd}_3\text{Sb}$ composition were found in Norilsk ores. A wide isomorphizm between Pt and Pd is established in the system, in particular within $\text{Pt}_3\text{Sn-Pd}_3\text{Sn}$ series. The minerals very often contain Au as an admixture up to 6 wt.% (Fig. 1). An almost complete isomorphism between Sn, Pb, As and Sb is found. Chemical isomorphism is expressed in terms of zonal occurrences of the minerals during successive growth and replacement.

Figure 1: Chemical composition of $\text{Pt}_3\text{Sn-Pd}_3\text{Sn-Pd}_3\text{Pb-Pd}_3\text{Sb-Pd}_3\text{As}$ minerals from Norilsk ore.

Does aerosol alter entrainment mixing in warm cumulus?

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We analyze the cloud microphysical response to entrainment mixing in warm cumulus clouds observed from the CIRPAS Twin Otter during the GoMACCS field campaign near Houston, TX in summer 2006. Cloud drop size distributions and cloud liquid water contents from the Artium Flight phase-Doppler interferometer in conjunction with meteorological observations are used to investigate the degree to which inhomogeneous versus homogeneous mixing is preferred as a function of height above cloud base, distance from cloud edge, and aerosol concentration. Using four complete days of data during which 101 non-precipitating cloud penetrations (minimum 300 m in length), we find that inhomogeneous mixing primarily explains liquid water variability in these clouds.

While theory predicts the potential for aerosol to affect mixing type via changes in drop size, over the range of aerosol concentrations experienced (moderately polluted rural sites to highly polluted urban sites), the observations, while consistent with this hypothesis, do not show a statistically significant effect of aerosol on mixing type. Instead we find two non-aerosol effects primarily control the microphysical response to entrainment mixing. First, we show that there is a tendency for mixing to be more homogeneous towards cloud top, which we attribute to the combination of increased turbulent kinetic energy and cloud drop size (due to condensational growth) with altitude which together cause the Damköhler number to increase by a factor of between 10 and 30 from cloud base to cloud top. Second, we find that cloud edges appear to be air from cloud centers which have been diluted solely through inhomogeneous mixing. We give plausible explanations for this second effect, but none thus far has been demonstrated using the observations.

Lastly, we discuss the possible ramifications of these observations on other key cloud properties, in particular warm rain formation and cloud albedo.
Formation of diamond from oxidized fluids/melts: $\delta^{13}$C-N SIMS study of an eclogitic diamond from the Jericho kimberlite, Canada

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Diamonds are key to understanding the sources, speciation and cycling of carbon in the mantle, and together this information is crucial for the study of mantle redox processes. The carbon isotope composition of diamond provides essential information on both the source and redox-state dependent speciation of C reservoirs involved in diamond growth. Growth models are commonly based on xenocrystic diamonds sampled from kimberlites and usually represent mixed populations and multiple growth events. In contrast, in situ studies of single growth zones in individual diamonds are better suited for building diamond growth models. Here we present the results of a coupled CL-imaging and SIMS $\delta^{13}$C-N study of a single, 0.5cm diamond from an eclogite xenolith from the Jericho kimberlite, Canada.

CL images of the diamond show a relatively homogeneous core mantled by oscillatory dark and light growth layers towards the rim. SIMS analyses of carbon isotope composition and nitrogen content in the core show systematic and coupled variations: N decreases rimwards from ~5000 to 1000 ppm and $\delta^{13}$C increases from -4.1 to -2.7‰ in the same direction. We interpret these systematic co-variations to reflect fractional crystallization of diamond from a single melt/fluid pulse. Moreover, the coupled rimward enrichment in $^{13}$C and depletion in N indicate diamond formation from an oxidized growth medium where N behaved compatibly in diamond relative to the medium. Modelling the core zone growth shows that the initial $\delta^{13}$C value of the diamond-forming fluid/melt was between -2.3 and 0‰ (depending on temperature and C speciation, e.g. CO$_2$ or CO). The carbon source therefore was either subducted carbonates ($\delta^{13}$C-0‰) that had undergone partial decarbonation causing $^{13}$C depletion or primary mantle fluids/melts (-5‰) that had undergone extensive C fractionation prior to precipitation of the diamond investigated here. We favor a model where the carbon was sourced from a carbonatite-like medium, potentially derived from subducted sediments, as the host eclogites themselves have evidence for crustal protoliths and interaction with carbonatite-like metasomatic agents.

Biotic dissolution of Tl(I)jarosite by *Shewanella putrefaciens* CN32

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Jarosites ($\text{MFe}_3 \text{(SO}_4)_2 \text{(OH)}_6$) are precipitated in the Zn industry to scavenge iron, alkali metals and sulfate ions during base metal processing and often contain toxic metals such as Pb, Ag and Tl. During this process, large volumes of jarositic wastes are produced and often confined to large repositories. Despite the toxicity of Tl, few studies exist on the abiotic and biotic dissolution of thallium mineral phases. In this study we examined the dissolution of synthetic Tl (I)-jarosite ($\text{TlFe}_3 \text{(SO}_4)_2 \text{(OH)}_6$) by *Shewanella putrefaciens* CN32 using batch experiments under anaerobic circumneutral conditions.

ATP, Fe and Tl concentrations were measured over time and showed increased Fe(II) and Tl in inoculated versus control samples (Fig 1). Tl concentrations in inoculated samples increased by a factor of 2 compared to control samples (Fig 1). In contrast to previous studies with Pb and Ag-jarosite, SEM images of *S. putrefaciens* CN32 did not show precipitation of Tl nanoparticles associated with the cell surface thus suggesting an alternative mechanism for Tl detoxification [1, 2].

**Figure 1:** Fe and Tl release over time

Volcanism on Methana (W Aegean arc): Magma mixing, crustal contamination & mantle sources

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The peninsula of Methana represents the westernmost active centre of the (continental) South Aegean arc. Volcanism started about 1.1 Ma ago and the last eruptive phase is as young as 2200 years. Volcanic deposits are mostly andesitic to dacitic lava domes and flows with abundant mafic enclaves, but two volcanic centres also show volumetrically important pyroclastic deposits [1].

The many mafic enclaves in the lavas suggest that magma mingling has been important. Evidence for magma mixing includes a poor correlation between modal mineralogy and silica content, and the common occurrence of disequilibrium assemblages (such as biotite, zircon, quartz + olivine). Major and trace element concentrations of different lava flows and domes show a large variability, seemingly unrelated to silica content. 87Sr/86Sr ratios are variable (0.705- 0.708), and the correlation with silica content is poor.

Enclosed xenoliths are mostly carbonates (and a few silicates) and are restricted to the two volcanic centres that also show pyroclastic activity. 87Sr/86Sr isotope ratios of these volcanics increase with increasing Sr concentration, suggesting carbonate assimilation. Interestingly, carbonate contamination is only observed in the pyroclast-bearing centres, and could therefore be responsible for their more explosive behaviour, as already suggested for Merapi volcano in Indonesia [2].

One lava flow displays a combination of the highest Sr concentrations (530 ppm, versus 200-350 ppm for the other volcanic deposits) and the lowest 87Sr/86Sr ratios (0.705). Similar volcanics have been found on the islands of Aegina and Nisyros, and point towards variations in mantle sources.

Uranium in tap and groundwater – Indications for anthropogenic origin

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Uranium (U) is a natural chemo- and radiotoxic heavy metal. The exposure of humans to U is mainly determined through uptake by drinking water. This paper reports on the U content in 4251 tap waters and 350 groundwaters from Germany collected by several research groups over the last 5 years and discusses the possible origin of U. This database is by far the largest available in the country and it represents data of drinking water to which 76% of the entire German population has access. The mean U concentration was 1.61 µg/L U, the median 0.50 µg/L U. 25.2% of all samples had U concentrations below the detection limits, which accounts for water to which 41.0% of the entire population has access. 24% of samples were above 2 µg/L U, 4.4 above 10 µg/L U, representing a population of 10.2 and 0.28%, respectively. The regional distribution of U concentrations follows the geological structures reported for mineral waters, however in contrasts to this clear evidences for anthropogenic influence through agricultural activities were found in drinking and groundwaters of areas with intense cropping productions in southern and northern Germany. Soil analyses show the high mobilisation capacity of fertilizer-derived U from arable soils in comparison to unfertilized control sites.

Processes of heavy metals immobilization in mires

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Long time mining and smelting activities have produced a widespread regional anomaly in Pb, Zn and Cd concentration in soils of Silesia region, southern Poland. Two mires: Bagno Bruch (BB) and Bagno Mikoląska (BM), located within the anomaly, were chosen to study processes of heavy metals immobilization in acid, water-logged and peat accumulating ecosystems.

The chemical analyses of peat were conducted using ICP-MS method. The solid samples (inorganic particles and peat) were investigated using FESEM.

A narrow peat layer, highly enriched in Pb, Zn and Cd, were detected at depth between 9 and 27 cm below the mires surface. The contaminated layer contained 460-1190 mg/kg of Pb, 1037-2371 mg/kg of Zn and 11.92 - 62.6 mg/kg of Cd. Above and below the layer, metal concentrations were several times lower, reaching values of 0.3- 8.0 mg/kg Pb, 22- 73 mg/kg Zn and 0.1- 0.5 mg/kg of Cd in the deeper (below 50 cm), pre-industrial peat layer.

The study shows that an important part of the contaminants are immobilized in inorganic particles. In the contaminated layer, the fly-ash particles, originated from dust deposition, comprise up to 1.7% by volume of dry peat. The formation of authigenic (Zn, Cd)S (up to 1.1% by vol.), barite (~0.5% by vol. in BB, not found in BM), and traces of PbS, indicates the importance of secondary processes, like microbial activity, in metals distribution and immobilization.

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Deformation of garnet in eclogite: Dominant mechanisms and the active role of fluids

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The response of subducting rocks to stress under different physicochemical conditions is crucial to predicting the evolution of slab strength and the generation of earthquakes. Experiments on mafic rock rheology [1, 2] suggest that prograde metamorphism to eclogite should not significantly change bulk-rock viscosity. Yet, field evidence demonstrates a dramatic, but temporary competence loss as a result of such reaction [3]. This discrepancy underscores the need for further study into the relationship between fluid-flow, mineral reactions, and rheological properties of eclogite.

Garnet fabrics are particularly enigmatic features that sometimes indicate very efficient deformation of this mineral under conditions where it is expected to remain rigid. To investigate this, we compared the textural and microstructural characteristics of garnet in an eclogite mylonite (Caledonian eclogites, Norway) to those of garnet that crystallized statically in a high-pressure seismic melt (Zambian eclogites).

In contrast to the static garnet crystals, mylonite garnet is flattened parallel to the main foliation. The grains exhibit foliation-perpendicular fractures, random crystallographic orientations, and abundant dissolution features, indicating mass transfer away from the grain boundaries. The grains accommodated large strains by intergranular pressure solution in the presence of fluid at high pressure.

This study shows that fluid-wetted grain boundaries occur in eclogite at depth and that these play a crucial role in the rheological weakening of such rock. Seismic imaging monitors the slab depth at which such weakening occurs as a distinct perturbation, beyond which slab coherence is strongly reduced [4]. Even though fluid invasion may be only short-lived [5] and eclogites should rigidify when fluids exit the system, the temporary competence loss of these rocks could have a great impact on slab dynamics.

Fractionation of a hydrous arc magma: The origin of adakitic and alkaline signatures at Savo volcano, Solomon Islands

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Savo, Solomon Islands, is a historically active volcano dominated by sodic, alkaline lavas and pyroclastic rocks with up to 7.5 wt % Na₂O, and high Sr arc-like trace element chemistry. The petrogenetic history of the erupted suite suggests high water contents in the parental melts, favouring: a) the early fractionation of oxides; b) early, abundant crystallisation and differentiation of hornblende; and c) limited extraction of feldspar. Instead, it shows pseudo-closed system crystallisation; plagioclase forms but does not fractionate, so although crystals record formation in a melt of decreasing Sr, whole rock Sr increases with magmatic evolution [1].

Early amphibole fractionation and limited plagioclase fractionation contribute to an adakite-like geochemical signature of the Savo suite. Previous authors have noted this [2], but in the case of Savo, the adakite signature is a consequence of the fractionation history. The sodic, alkaline nature can also be attributed to feldspar; whole rock Na increases with SiO₂ as albite is retained. Na/K increases by biotite fractionation.

Much of the magma’s water load appears to be released prior to eruption; Savo’s eruptive style is that of dome formation, and pyroclastic rocks are all crystalline and non-vesicular. Fluids are released to a hydrothermal system [3] with the potential to form economic mineralisation. The oft-made linkage between “adakitic” magmatism and economic copper and gold mineralisation (see [4] for review and criticism) may instead be an association between mineralisation and hydrous parental magmas.

Monogenetic basaltic volcanoes represent extraction rather than melting events

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Magmas from very small basaltic systems (volumes <0.1 km3) leak from the mantle on time scales of 104-106 years to form fields of small volcanoes each resulting from a single short-lived eruption sequence. Because magma volumes are small and rise quickly they do not fractionate within the crust or assimilate components from it. Hence, their chemical compositions and variability reflect the interplay of processes deep in the system. The range of chemical compositions displayed by individual eruptions shows the diversity of these processes. Do these small magma batches represent discrete melting events or instead extraction episodes tapping long-lived (104 year) zones of partial melting? In the Auckland Volcanic Field N.Z. paleo-magnetic measurements [1] correlated with the ~ 31 ka Mono Lake magnetic excursion identify five eruptions of alkali basalt magmas from depths of ~80 km within a time interval of a few hundred years. The chemical composition erupted in each event cannot be related to the others by fractionation processes. Heat flux constraints suggest that these discrete magma batches cannot represent distinct melting events. Rather they represent separate extraction events from a continuous but heterogeneous melt zone. Their near simultaneous eruption along with the overall pattern of volcanic activity at Auckland indicates that such extraction events may be driven by plate boundary related tectonic processes occurring over 600 km away.


Australasian sea surface temperatures over the past millennium

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The ‘hockey-stick’ temperature increase of the 20th century has instigated concern for a global warming trend. In order to investigate this temperature increase, it is necessary to derive high-resolution temperature records that span the last millennium. Currently, data from this period is sourced almost exclusively from the Northern Hemisphere, predominantly from terrestrial records. There is a considerable lack of temperature records for the Southern Hemisphere, making analysis of hemispheric and global trends in temperature changes difficult.

Marine sediments can often represent a continuous geological record of climate through the gradual deposition of organic matter on the sea floor over time. Biomarkers are organic compounds produced by living organisms that have extraordinary preservation potential in sediments. The most useful biomarkers are resistant to diagenesis and can be readily linked to a characteristic group of producing organisms [1]. The lipids of some haptophyte marine algae (alkenones) and marine Crenarchaeota (glycerol dialkyl glycerol tetraethers) in the sedimentary record are biomarkers that may be converted to sea-surface temperature via the UK-37 [2] and TEX86 [3] proxies, respectively.

Here, we present a record of sea-surface temperature using multicores sourced from near the Australian east coast (at ~1,000 m depth) utilising the combined capacities of these biomarker proxies. This is the first temperature record to span the past millennium in the Southern Hemisphere and provides an important means of palaeoenvironmental inference for hemispheric and global climatic trends during this period.

Mercury isotope fractionation in layered roasted ore waste

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High concentrations of mercury (Hg) can often be found in the environment around inactive Hg mines. During mine operation, rock containing the primary ore mineral HgS was crushed and heated in furnaces to temperatures of ~700 °C (calcination). Most of the resulting elemental Hg vapor was condensed and collected and the remaining mine tailings (calcines) were piled on site. This removal process was not complete and significant amounts of Hg remained in the calcines. Large pieces of calcine often exhibit a characteristic internal layering, with dark-grey cores, light-grey outer rims, and red outer surface layers. The speciation of the Hg-bearing compounds in these wastes determines the solubility, volatility, and thus mobility of the remaining Hg [1, 2].

Various environmental processes fractionate the stable Hg isotopes via mass-dependent (MDF) and/or mass-independent fractionation (MIF); however, the controlling mechanisms are not fully understood. These isotopic signatures provide a promising new tool for further understanding Hg transformations and emissions from highly contaminated mining sites. Here we report stable Hg isotope results for different layers in calcine cobbles collected at the inoperative New Idria Hg mine, San Benito County, CA, USA.

Differently colored layers in the calcines were carefully separated, powdered, and digested following either total or sequential procedures [3]. Isotopic analyses were performed on a Nu Plasma MC-ICP-MS with cold vapor introduction.

Our analyses revealed significant concentration gradients across the different layers, with higher Hg concentrations in outer rims and lower concentrations in inner regions. In all sequential extractions, the 12M HNO3 soluble fraction displayed the highest Hg concentration. In general, bulk calcine samples were isotopically heavier than ore and unroasted ore wastes, and significant MDF δ203Hg gradients existed from isotopically heavy centers to lighter rims. These findings suggest that incomplete roasting of ore rocks led to pronounced Hg isotope gradients which were presumably caused by kinetic effects during diffusive processes.


Toward establishing precise chronologies for the integration of Late Pleistocene palaeoclimate archives: An example from Suigetsu SG06, Japan

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To further understand abrupt climate changes, and any geographical leads and lags, it is important to precisely correlate high-resolution terrestrial, marine and ice core archives from around the globe. This requires improved dating techniques and methods for correlating these sedimentary archives. Volcanic ash (tephra) layers provide ideal markers to synchronize records over regional areas, and 40Ar/39Ar eruption ages can provide direct temporal constraints. Here we discuss the methodology used to obtain high-precision 40Ar/39Ar age of a tephra within the SG06 Suigetsu archive.

The 73 m-long SG06 core from Lake Suigetsu, Japan provides continuous record of sedimentation spanning the last ~150 kyrs [1] and represents one of the most important Late Pleistocene palaeoclimatic records. SG06 is annually layered (varved) down to ~65 kyrs and contains numerous terrestrial plant macrofossils, from which a varve chronology and radiocarbon analyses are currently being paired to generate a wholly terrestrial radiocarbon calibration dataset that extends to the older limit of the radiocarbon analytical method (see [1]). We present our 40Ar/39Ar ages along with the varve and 14C chronology to show that it is possible to get accurate and precise ages of eruption units that are near the young limit of the 40Ar/39Ar method.

The scale factor in the ectomycorrhizal fungal weathering debate

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Ectomycorrhizal fungal weathering research has a long history, but with the launch of the term ‘Rock-eating Fungi’ this research topic attracted increased attention. There is growing evidence that ectomycorrhizal fungi do interact with soil minerals. Carefully designed laboratory experiments show increased mineral dissolution rates in the presence of ectomycorrhizal fungi. Even at the scale of the individual hyphae we gain more insight in the mechanisms of fungal-mineral interactions via sophisticated (ultra-)microscopic and spectroscopic techniques. But the basic question whether ectomycorrhizal fungi have a significant contribution to soil mineral weathering, remains unanswered.

Over the past decades several reviews have been published, some advocating and others opposing the role and significance of ectomycorrhizal fungi in soil mineral weathering. Most of the arguments used in this debate are scale-dependent. The ignorance of the importance of scale has hindered communication and better insight into each other arguments. Key points in the arguments opposing ectomycorrhizal weathering are that mineral dissolution is expected to be mainly driven by water or proton-metal exchange reactions and not through the formation of organic-metal complexes due to extremely low concentrations of organic chelators in soil solutions. Key points in the arguments in favour of ectomycorhizal weathering are that fungi act at the scale of individual hyphae, creating isolated water pockets with probably very distinct chemistry and showing hyphal-mineral contact interactions.

It is important to realize that in ectomycorrhizal plants, the fungal partner is the main interface between plant and soil. Recent studies show that fungal hyphae preferentially colonize some minerals over others, implicating that plant/fungal interactions with minerals take place in a nonrandom fashion. But fungal hyphae only cover <5% of the mineral surfaces. The scale and heterogeneity of weathering actions should be acknowledged before drawing conclusions in relation to the relevance for the actual soil mineral weathering process.

Excess argon systematics under HP-LT conditions: A tracer for metamorphic fluid connectivity?

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UV laserprobe single-grain fusion apparent 40Ar/39Ar ages of phengite from a gl + jd bearing blueschist of the Tauern Window, Eastern Alps range between 35.35 ± 0.37 Ma and 43.67 ± 0.50 Ma (1σ). These ages are between 2—11 Ma older than the age of blueschist-facies metamorphism determined by U—Pb allanite [1] and Rb—Sr [2] multi—mineral geochronology. Pseudo-section calculations show that the phengite grew close to peak pressure conditions of ~10 kbar at 450° C, before Barrovian metamorphism (~7 kbar, 550°C) at ca. 30 Ma [3]. The anomalously old 40Ar/39Ar phengite ages show that the sample contains excess 40Ar, i.e. 40Ar decoupled from parent 40K. Concentrations of excess 40Ar vary on the mm—cm lengthscale.

The incompatible nature of Ar means that high concentrations of fluid—borne Ar are required to facilitate partitioning of Ar into mica. Numerical modelling of Ar diffusion in phengite provides an estimate of the expected 40Ar/39Ar age for a mica following the Tauern PTt path. We show that the measured ‘older’ apparent ages may be reproduced by: 1. an open rock volume, where Ar is fluid—borne within an interconnected grain boundary reservoir, 2. a closed system in which the Ar concentration of the grain boundary reservoir is controlled by metamorphic porosity and whole—rock K2O content, or 3. a temporal variation between these two end-member scenarios. Collectively, these calculations show that, provided an independent constraint on the timing of mica growth exists, excess 40Ar contamination can be used to investigate degrees of fluid flow and fluid pathway connectivity during a metamorphic cycle.

Hydrous phases in the lower mantle

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Dehydration of subducting lithospheric slabs to less than 200 ppmw H2O in the upper mantle is virtually impossible given the stability of nominally hydrous phases such as serpentine, 10Å phase, phase A, chondrodite, and clinohumite. Velocity models of the transition zone are consistent with significant hydration (> 1000 ppmw H2O), but not with a dry pyrolite composition. It seems likely then that transition zone is relatively hydrous and that slabs penetrating the TZ are also hydrous. Where slabs push through 660 km into the lower mantle the fate of the water depends on the H solubility in MgSiO3-perovskite, periclase, akimotoite, and majoritic garnet as well as the nominally hydrous phase D.

FTIR studies indicate relatively low solubility of H in perovskite and periclase [1]. However, we have synthesized MgSiO3-perovskite with up to 2000 ppmw H2O as measured by SIMS. It is, however, as yet unclear if the H is in the structure or as inclusions. We have measured up to 3000 ppmw H2O in majoritic garnet where hydration may be associated with Mg octahedral vacancies. Phase D (MgSi3H2O6) is a nominally hydrous phase stable to depths up to 1500km. We have synthesized Phase D in silica-excess and Mg-excess compositions as well as aluminous compositions. Phase D has a high bulk modulus but a relatively low density so that hydrous slabs penetrating 660 km may be buoyant [2]. Further experimental work is required for a meaningful constraint on possible H contents of the lower mantle.


Hot summers in the Western United States during the Late Cretaceous and Early Cenozoic

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Understanding how seasonal temperatures on land respond to global greenhouse climate conditions is important for predicting effects of climate change on ecosystem structure, agriculture and distributions of natural resources. Fossil floral and faunal assemblages suggest winter temperatures in middle and high latitude continental interiors during the Cretaceous and early Cenozoic were at or above freezing, whereas terrestrial summer temperature estimates are uncertain. Carbonate clumped isotope ($\delta^{18}C$) temperature estimates from lacustrine and paleosol carbonates appear to be generally biased toward summer temperatures in middle and high latitudes. Though problematic for reconstructing mean annual temperature (MAT), this bias presents an opportunity to reconstruct terrestrial summer temperatures and, through comparison with paleobotanical data, estimate past terrestrial seasonality.

Here, we compile MAT estimates from paleoclimate and paleoelevation studies in the western United States. We then compare these data with existing [1, 2] and new $\delta^{18}C$ temperature estimates from Late Cretaceous – Present lacustrine and paleosol carbonates from the western United States. In this compilation, land temperatures are warm during the Late Cretaceous, reach an apex during the early-middle Eocene and then cool to the present (sharply from the late Miocene to Pleistocene). Both MAT and summer temperature estimates are warmer than modern MAT and summer temperature estimates at the study sites throughout the Cenozoic and Late Mesozoic. Summer temperatures from low paleoelevation sites during the Late Cretaceous to the Early Eocene are relatively warm (~30 – 40°C), though these values may include a few degrees of radiant solar heating of the surface. Regardless, these data suggest that at middle latitudes, both winters and summers in continental interiors may warm substantially under greenhouse climate conditions.

Anthropogenic contributions of $^{129}$I and $^{85}$Kr to global reservoirs: Current distribution patterns and projected increases

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$^{129}$I and $^{85}$Kr are two isotopes whose presence in global surface reservoirs is due primarily to nuclear reprocessing activities. A knowledge of the partitioning of these isotopes in surface reservoirs is critical to our understanding of how release and storage of these isotopes should be handled presently and in the future.

Long-lived $^{129}$I (half-life=15.6 Myr) partitions primarily into shallow soil and seawater. While its residence time in the atmosphere is short, repeated cycling of iodine between surface waters and the atmosphere has resulted in its distribution far from point sources. Downwelling of surface waters in the North Atlantic presently transports $^{129}$I to deep waters which provide a temporary sink for anthropogenic iodine. In contrast, the relatively short-lived $^{85}$Kr (half-life=10.76 yr) partitions primarily into the atmosphere and its dispersal is a result of wind patterns in the troposphere. We compare the present distribution of these two isotopes and model their increase into the future when the bulk of nuclear reprocessing is projected to move from Western Europe to Asia. We also discuss the effect of speciation of $^{129}$I and stable $^{127}$I in the environment, and disequilibrium between these two isotopes.

Combined use of Raman, ToF-SIMS and AFM imaging for characterizing the surface reactivity of sea salts

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Sea salt particles are typically emitted in the atmosphere through by breaking waves and bursting bubbles at the ocean surface where Cl$^{-}$, Na$^{+}$, Mg$^{2+}$, K$^{+}$ and SO$_4^{2-}$ are the most abundant ions. It is well established that sea salts can react with gaseous species to form complex aerosols [1, 2]. Such reactive uptakes on the surface of particles during their atmospheric residence time can significantly alter their optical properties and affect their ability to act as cloud condensation nuclei. In addition, some products may be photochemically active at solar wavelengths and may affect the oxidative properties of the atmosphere [3]. Finally, in the marine atmosphere fatty acids (FA) are known to be present as particles and/or as a coating on sea salt particles which could influence sea salt reactivity [4]. In situ observation of the atmospheric processing of the surface of particles can be performed in laboratory by Raman microspectrometry (RMS) and Atomic Force Microscopy. The combined use of both techniques is a powerful tool to determine the morphology and the distribution of molecular species within individual micrometer-size particles [5]. Moreover, the first layers at the surface of particles (few nm) can be analyzed using Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) [6]. In this study, laboratory experiments were conducted to simulate heterogeneous reaction at the surface of sea salt particle (NaCl) coated with FA and exposed to gaseous pollutants (NO$_x$). As expected, formation of nitrate salts on the surface of NaCl was evidenced and influence of FA demonstrated at the surface scale. Finally, by using RMS imaging in the UV range (266 nm and 325 nm), the photochemistry of formed nitrates and influence of FA on their photo-reactivity was also studied. This work demonstrated the the potential of the combination of RMS, AFM and ToF-SIMS imaging for studying the heterogeneous chemistry of the particle surfaces.

Mineral composition of sediments of the Southern Baltic Sea and their heavy metals content

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Samples of sediments were collected from eight cores in three areas of the southern Baltic Sea (the Gulf of Gdańsk, Bornholm Deep and the Odra Bank) from three different depths (0-3cm, 25-28cm and 35-38cm).

Mineral and chemical composition of sediments was studied using XRD, SEM-EDS, ICP-MS, and ICP-AES methods. Chemical composition of leachates from sequential extraction was also determined.

Samples from the Gulf of Gdańsk are dominated by silty fraction, samples from the Odra Bank represent fine to medium sands with abundant shell fragments, sediments from Bornholm Deep are mainly clay. Quartz predominates in all samples. In silty samples framboidal pyrite is present; halite and gypsum occurs only in few of them. Clay minerals occur in low amount in silty samples. Ilmenite, zircon and Fe compound are common in sand, but appear sporadically in silt samples.

Geoaccumulation index (Igeo = ln (Cn/1.5Bn); Cn - measured concentration, µg/g, Bn - geochemical background value, µg/g) indicates strong to very strong Cd pollution in three surface samples. Other factors revealed pollution by As, Cd, Mo and Hg. Variation of concentration of heavy metals occurs in profiles, e.g. Hg and Cd are concentrated in uppermost samples but As and Mo concentration increase downward. Results of sequential extraction suggest significant diversity of metals speciation in sediments.

Crustal recycling: New findings and challenges

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Since Hofmann and White’s paper [1] crustal recycling via subduction and convection is a widely accepted explanation for the heterogeneity of OIB sources. Recycled crust has been recognized even in the sources of MORB (e.g. [2, 3]). However, there are still no common view on the amount, composition and ages of recycled materials in both parts of the mantle.

In this paper I review recent approaches for estimating the contents and ages of recycled crust in the sources of OIB, LIP and MORB. In particular, I discuss the ability of olivine phenocrysts to record the magma source mineralogy in their concentrations of Ni, Mn, Fe, Zn, Co, Sc and Ca. I show that adiabatic decompression of deep-sourced mantle magmas and the presence of garnet in their sources do not compromise the ability of olivine to register olivine-free source lithologies.

Large datasets of new olivine compositions and published high-precision analyses [3, 4] suggest the common presence of olivine-free pyroxenite produced by melting and reaction of oceanic crust in the sources of OIB, LIP and MORB. The proportions of pyroxenite-derived melt commonly correlate with trace element and isotope data from bulk rocks [5, 6] indicating binary mixing of melts from peridotitic and pyroxenitic sources. High amounts of recycled oceanic crust are associated with high excess mantle temperatures and high depths of melt generation, in agreement with the high density and melt productivity of a garnet-rich source [3].

The ages of recycled oceanic crust estimated from correlation of bulk-rock ¹⁸⁷Os/¹⁸⁸Os ratios and the proportions of pyroxenite-derived melt [5] or from the ⁸⁶Sr/⁸⁷Sr of ancient recycled seawater [7] are in the range of 1.0-0.2 Ga. This implies a time-scale of general mantle circulation of a few centimetres per year.

Heterogeneities in the mantle plume: Spatial scales and ages  
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Recycling of oceanic crust through subduction, mantle upwelling, and remelting in mantle plumes is a widely accepted mechanism to explain ocean island volcanism. However, neither time scales of this process nor spatial scales of the resulting mantle heterogeneities are well understood.

We report data on trace elements, 87Sr/86Sr, 207Pb/206Pb, and 208Pb/206Pb ratios for 138 melt inclusions in olivine phenocrysts from single lava of Mauna Loa shield volcano, Hawaii, indicating enormous mantle source heterogeneity. The variations in isotopic compositions and trace element ratios far exceed all known ranges for Hawaiian shield stage volcanoes. The variation range is highest for melt inclusions trapped in the most magnesian olivines. This is consistent with the interpretation that melt inclusions in early olivine phenocrysts yield information on the compositions of unmixed parental melts, while lavas and inclusions in more evolved olivine are mixtures of these melts.

We show that highly radiogenic strontium (87Sr/86Sr=0.7081± 0.0006, 2σ) in severely Rb-depleted melt inclusions matches the isotopic composition of 200-650 Ma old seawater. We infer that such seawater must have contaminated the Mauna Loa source rock, prior to subduction, imparting a unique ‘time stamp’ on this source. Small amounts of seawater-derived strontium in plume sources may be imparting a unique ‘time stamp’ on this source. Small amounts contaminated the Mauna Loa source rock, prior to subduction, Old seawater. We infer that such seawater must have

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We also show that the Sr-rich component of Mauna Loa lavas is particularly unradiogenic (87Sr/86Sr < 0.7030), supporting the suggestion that it corresponds to plagioclase cumulate gabbros from recycled oceanic crust (Sobolev et al., Nature, 2000).

Enormous isotope heterogeneity of melts mixed in a single plumbing system favours small-scale mantle source heterogeneity preserved in the mantle plume. The presence of 200-650 Ma oceanic crust in the source of Hawaiian lavas implies a time-scale of general mantle circulation with an average rate of about 2 (± 1) cm/a, a much faster rate than previously thought.

Modeling relationships between a mantle plume, a large igneous province and a mass extinction  
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Large Igneous Provinces (LIPs) are known for their rapid production of enormous volumes of magma, for dramatic thinning of the lithosphere and for their links to global environmental catastrophes. Controversy surrounds even the basic idea that LIPs form through melting in the heads of thermal mantle plumes. The Permo-Triassic Siberian Traps – the type example and the largest continental LIP, is located on thick cratonic lithosphere and was synchronous with the largest known mass-extinction event. However, there is no evidence of pre-magmatic uplift nor of a large lithospheric stretching of the basaltic sequence, predicted above a plume head. Moreover, estimates of magmatic CO2 degassing from the Siberian Traps are considered insufficient to trigger climatic crises leading to the hypothesis that the release of thermogenic gases from the sediment pile caused the mass extinction.

Here we present petrological evidence for a large amount (15 wt%) of dense recycled oceanic crust in the head of the plume and developed a thermomechanical model that predicts no pre-magmatic uplift and requires no lithospheric extension. The model employs source-composition and temperature [1, 2] petrological constraints, non-linear elasto-visco-plastic rheology [3] and pressure- and temperature-dependent melting of a heterogeneous mantle. The model implies extensive plume melting and heterogeneous delamination of the thick cratonic lithosphere during a few hundred thousand years. The model also suggests that massive CO2 and HCl degassing from the plume could alone trigger the Permian-Triassic mass extinction and predicts it happening before the main volcanic phase.


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The effect of pressure on tetrahedral tilting in feldspars

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Feldspars are framework aluminosilicates that comprise approximately 60 percent of the Earth’s crust. The defining features of the feldspar framework are corner-sharing TO₄ tetrahedra connected into chains of 4-rings that run parallel to a-axis and b-axis. These 4-rings are connected by their corners and form a ‘double-crankshaft’ chain parallel to the d (100).

The response of the feldspar structure to pressure is very anisotropic with approximately 60-70% of the volume compression attributed to the length of the crystallographic direction d (100) [1]. It is of interest to undermine the details of this anisotropy and to predict thermodynamic properties and phenomena such as elastic softening for petrologic and geophysical investigations. Previous attempts to predict structural behavior of feldspars have been focused on individual T-O-T angles [2, 3], but this has been unsuccessful in describing structural reasons for either changes or the thermodynamic properties. Megaw (1974) [4] proposed a model that considers four independent tilt systems derived and 2 of the four tilt systems effect the length of the d (100).

Single crystal X-ray diffraction was performed on an ordered plasioclase crystal of 20% anorthite content and structures were determined from 0 – 9.221 GPa. The effect of high pressure on these four different tilt systems have been studied on Na-rich plagioclase from this study and previously measured samples from 0 - 37% anorthite. I found that 3 of the 4 tilt systems change similarly until 5-6 GPa. After this pressure range, these three tilt systems change behavior. Interestingly, these are the approximate pressures that there is elastic softening seen in the volumes for Na-rich feldspars.

Our mixing analysis focuses on finding the simplest model that fits the MORB and OIB isotopic data and is consistent with the wider body of geochemical evidence. This type of rigorous statistical method is indispensable for analyzing large amounts of complex geochemical data, and it provides an objective means for discriminating between competing models of mantle mixing through formal hypothesis testing.


A new statistical method for modeling mixing of mantle end-members for global MORB and OIB isotopic data

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Long-lived isotopic ratios have been used to identify reservoirs of chemically distinct material in the Earth’s interior, typically labeled DMM, EM1, EM2 and HIMU [1, 2]. We have developed a new statistical method that allows us to find best-fitting mixing curves and surfaces for binary and ternary systems, respectively, and we apply this method to global compilations of isotopic ratios (⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb) for MORB and OIB samples in order to rigorously test various mixing hypotheses. The method also allows us to refine isotopic ratio estimates for the putative mantle end-member components, and quantify the misfit between a given dataset and an arbitrary mixing model.

We find that the global suite of MORB data requires at least three end-member components, one of which is DMM, a second that is similar to EM1 but with distinct Pb isotopes defined by samples from the South Atlantic, and a third that is similar to, but nevertheless distinct from, HIMU, defined by samples from the equatorial Atlantic. The global suite of OIB data, on the other hand, requires at least five end-member components, four of which appear to mix with the common component FOZO [3, and references therein]. Some OIB sample sets (e.g. Hawaii, Iceland), however, are difficult to distinguish statistically from the MORB field.

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Protracted history of continental subduction at the southern edge of the Maya Block, central Guatemala: Petrological and geochronological evidences

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The Rabinal Granite Suite is an anatectic S-type composite pluton which fringes the southernmost North America Plate margin in Central Guatemala. It is a Kfs-Pl-Ms-Qtz granodiorite, showing increasing deformation along its southern margin where it is crosscut by the dextral, Late Cretaceous, top-to-NE Baja Verapaz Shear Zone. Previously considered as Devonian-Mississippian in age, it has been recently dated at 562-453 Ma. LA-ICPMS U-Pb and Ar-Ar geochronology, combined with microprobe mineral chemistry, allow precising its P-T-time history. U-Pb zircon ages indicate a crystallization age of 471 ±3/ -5 Ma (Middle Ordovician), as well as abundant cores inherited from the metapelitic source with main density peak distributions at 700, 806, 900, 996, 1376 Ma. Laser total fusion Ar-Ar analyses of magmatic muscovite (Si= 6.2-6.4 atoms per 20 O and 4 OH) indicate cooling at various times during the mid-late Paleozoic. The petrologic conditions of the Ordovician metamorphism, partial melting of a metapelitic protolith and segregation-ascent-crystallization of the granitic melt occurred along a clockwise P-T-t path at intermediate P, with maximum P of 8 kbar (ca. 25 km) during prograde metamorphisms and peak T of 750 °C (at mid-crustal levels, 5-7 kbar). This evolution is interpreted as the result of a tectonic cycle related to the initial opening of the Rheic Ocean. A second clockwise path at high-P is indicated by high silica muscovite (Si> up to 7.0 atoms pfu), with peak P of ca 10 kbar at ca. 330 °C. This second event did not recrystallize the U-Pb clock in zircons, but it is clearly recorded by a main peak of laser total fusion Ar-Ar analyses on high Si muscovite grains yielding an average of 70.09 ±0.5 Ma. This latest Cretaceous stage is related to subduction of the North America plate margin (cover and pre-Mesozoic basement) below the Caribbean Plate and ensuing collision with the Caribbean volcanic arc.

Evolution of magma oceans

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Lord Kelvin’s vision of the early molten Earth has been reincarnated after the samples returned by the Apollo missions presented evidence that the Moon might once have been molten. This evidence led to a hypothesis of a lunar magma ocean. The idea of an early molten Earth - the terrestrial magma ocean hypothesis - was developed not long after and rapidly gained a broad acceptance [1]. Magma oceans or magmaspheres of various types on Earth as well as on other terrestrial planets have been proposed [2-8]. The growing list of extrasolar planets now includes planets which currently are likely to be at least partially molten [9]. The hypothesis of magma oceans is undoubtedly among the most important building blocks in the modern narrative of planetary formation and evolution. The major challenge in describing the evolution of magma oceans is that we have to deal with the extreme conditions of planetary interiors where the material properties and global dynamics are poorly understood [10, 11]. Answers to even basic questions concerning whether solid phases sink or float in magma oceans, how long it takes magma oceans to crystallize and where chemical equilibration occurs have been eluding researchers for decades. Yet, these questions are critical for the interpretation of geochemical data, for the understanding of how magma oceans lead to the current planetary structures and to the current dynamic regimes of planetary interiors including the existence of plate tectonics on Earth [12].

Mobility of elements from cesium formate residue emplaced on pegmatite tailings

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A unique Cesium Products Facility (CPF) manufactures a cesium-formate drilling mud from pollucite ore at a pegmatite mine in SE Manitoba, Canada. The CPF is a closed system, with the waste slurry discharged to containment cells. When a cell is full, the Cs-rich slurry is dewatered, and the residue is dry-stacked on neutral tailings in a hydrogeologically closed tailings management area. This study concentrated on the geochemical and mineralogical reactions occurring within the residue pile and the underlying tailings to determine the mobility of Cs and other residue-related elements including Rb, Sr, Ba and Li.

Drill cores were extracted from the residue and tailings. The mobility of residue-related elements was examined through mineralogical observations, sequential extraction and porewater analysis.

The residue contains an order of magnitude more Cs (up to 2 wt. %) than the tailings (up to 0.3 wt. %). Sequential extraction results showed that 47% of the total Cs in the residue is mobile under natural conditions, compared with only 24% in the tailings. The stable forms of Cs in the residue are pollucite, feldspar and formate with sulphate and carbonate being the mobile forms. The Cs being released into the tailings does not appear to be re-precipitating in secondary phases. Cesium is predominantly in pollucite in the tailings. Rb, Sr, Ba and Li are all immobile in both the residue and the tailings in feldspar, lepidolite and barite.

Earth’s early atmospheric density revealed from Archaean raindrop imprints

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The Archaean atmosphere has been investigated dominantly by numerical models that typically assume a total atmospheric pressure of ~1 atm [1-3]. However, barometric pressure may have been different, owing to the negligible presence of oxygen in the atmosphere [4], and the resulting difference in the redox-sensitive cycling of the other major gas, nitrogen.

We have developed a new method that uses lithified raindrop imprints as a proxy for atmospheric density. We consider the physics that determine the morphology of raindrop imprints preserved in tuff of the ~2.7 billion year old Ventersdorp Supergroup of South Africa [5]. Volume and surface area of raindrop imprints are a function of raindrop size and terminal velocity, the latter being dependent upon air density, whereas maximum raindrop size is not.

We experimentally determine the relationship between imprint volume and surface area as a function of raindrop size in wet ash (10% moisture by weight) from the 2010 Eyjafjallajökull event (Iceland) and Pahala (Hawaii), as modern analogs to the Ventersdorp tuff. We are then able to place an upper bound on the late Archaean atmospheric density, which has previously had no such observational constraint.

‘WEERTMAN’ cracks:  
A possible mechanism for near sonic speed diamond extraction from the Earth’s mantle

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‘Weertman’ cracks are two-dimensional liquid-filled cracks, which can move with a velocity close to Rayleigh-wave speed driven by the buoyancy or gravitational potential energy of the fluid and external stress fields. Therefore ‘Weertman’ cracks would be a potential transport mechanism for the diamond bearing kimberlitic-melt from the Earth’s mantle to the Earth’s surface. Arguments for the formation of ‘Weertman’ cracks are threefold: i) The geometry of kimberlite pipes resembles the shape predicted by ‘Weertman’ cracks; ii) Like Weertman cracks Kimberlites themselves never develop an explosive stage besides the phreatomagmatic eruption due to contact with groundwater close to the Earth’s surface; the melt often gets trapped near the Earth’s surface; iii) The speed for the uplift of the diamonds from >150 km depth must be larger than 800 km/h to explain preservation of diamonds. The question to be answered is: What method can be used to confirm the formation of ‘Weertman’ cracks? Here we show that OH-diffusion profiles in nominally water free minerals, recorded from quenched diamondiferous host rock, are indicative for near sonic speed diamond extraction from the Earth’s mantle. This unforeseen discovery shows that ‘Weertman’ cracks are the only possible transport mechanism for diamonds from the Earth’s mantle to the surface. Further, our findings show that the observed breadths of kimberlitic pipes are surprisingly short, given the fact that the magma ascends from depths in order of up to ~330 m/s. The ascent rates of Kimberlites are of high economic interest, because if the diamonds are to long in contact with the kimberlitic melt they start to dissolve within a few minutes.

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Provenance discrimination of plants from three bedrock types using strontium isotopes and chemical analysis

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This study is to assess the inter-lithological variations in the stable Sr isotopes that define an ecosystem/habitat nutrient cycle and their signature in the aboveground vegetation. Five plant species, Acacia sp., Zelkova serrata, Prunus serrulata, Capsicum annuum, Zea mays and Allium fistulosum commonly found growing on granite, limestone and basalt formations were selected. Our hypothesis is based on the two facts-one the 87Sr/86Sr ratios depends on geological regime and this ratio varies significantly from one geological formation to another [1]. Second plants display particularly strong isotopic signals because they construct their tissues from such small molecules [2]. Based on these premise this natural phenomenon can be put into use to explain inter-lithological differences and effects of these inter-lithological variations on plant nutrient physiology.

Preliminary analsysis shows that 87Sr/86Sr ratios of tree leaves and fruit vegetables varied according to bedrock types in which they grow. 87Sr/86Sr ratios of plant leaves and vegetables well reflected the geological characteristics of three regions where they were grown.

Integrated model to simulate and predict fate and transport process of contaminant in vadose zone

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Interaction between surface water and groundwater is always a hot research topic in geochemistry, ecohydrology and interdisciplinary sciences. It’s better to reveal the law of contaminant behavior in the regional water cycle process coupling of surface water and groundwater simulation, and also provide a good basis for the comprehensive consideration in environment changes effected by nature and anthropogenic. Vadose zone is the bond linking of surface water and groundwater, therefore, the physical mechanism of integrated model will be greatly enhanced considering the dynamics of vadose zone water movement. In this research, the rural plain area in the Capital City of China, Beijing with water eco-system protection function has been selected as the study location which experiences period of drought and wetness annually. Based on the use of traditional field survey techniques combined with remote sensing technology to access to the model parameters, this research will discuss the comparison between two surface - groundwater integrated models (MIKESHE and IHM) to simulate and predict the fate and transport process of nitrogen loading in the study area.

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The molybdenum isotopic indication of low-medium temperature hydrothermal ore-forming systems: A case study on the Dajiangping pyrite deposit, Western of Guangdong Province, China

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We present molybdenum isotope data from 12 hydrothermal syndepositional silicalite and carbonaceous slate samples from the Dajiangping pyrite deposit in western Guangdong Province, South China. The $\delta^{97/95}\text{Mo}$ values from Orebody III range from -0.02‰ to 0.29‰, with an average of 0.18‰. In contrast, the composition values from Orebody IV display a larger variation from -0.70‰ to 0.62‰, especially the five samples from the main ore bed all show strong negative values. Orebody III is likely to have been deposited from submarine exhalative hydrothermal fluids under a relatively strong reducing environment and Orebody IV may have also been influenced by hydrothermal superimposition in a more oxidized disequilibrium condition. The $\delta^{97/95}\text{Mo}$ values of Orebody IV are clearly negative, together with the values increasing stratigraphically upward in the ore beds, suggesting that the metallogenic environment of Orebody IV could be present dynamic fractionation in this restricted environment. Microorganisms including organic matter and replacement and/or adsorption of Fe-Mn oxides might influence the Mo isotopic fractionation in the ore-forming fluids.
Structural controls on surface hydroxyl reactivity in iron hydroxides

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Mineral surfaces are populated with distinct types of hydroxyl groups displaying various catalytic roles with respect to gases, solvents and solutes. Knowledge of the types and distributions of hydroxyl groups on minerals with different surface structures is essential for gaining molecular-scale resolution of these processes.

This work provides Fourier transform infrared (FTIR) spectroscopic signatures of hydroxyl groups present on surfaces of FeOOH minerals, including lath- and rod-shaped lepidocrocite (γ), (nano) goethite (α) and akaganéite (β).

Figure 1: Synopsis of FTIR work, assisted by MD simulations, used to identify surface species and reactivity.

Our combined FTIR and molecular dynamics studies of these FeOOH surfaces enabled the extraction of unique spectroscopic signatures for distinct hydroxyl groups. Individual responses of these groups to variations in proton loadings and temperature provide experimental validation to previous theoretical accounts on their reactivity. These efforts now provide new possibilities for probing important gas-phase adsorption processes. They should moreover lay foundations for interfacial studies involving water.

La-Ce and Sm-Nd isotope geochemistry of felsic granulite in the Jirisan complex, Yeongnam Massif, Korea

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REEs contain two long-lived decay systems, the 147Sm-143Nd and 138La-138Ce decay systems, which provide us with the information on ages and initial ratios that helps us understand their origin and history. Hence, the application of the La-Ce and Sm-Nd isotope systematics in petrogenetic studies has enabled an estimation of the light rare earth element (LREE) patterns in source materials of the rocks.

We report La-Ce and Sm-Nd isotopic data of highly evolved granites with the composition of major and rare earth element from the felsic granulite, which occurs at the Jirisan Complex in the Yeongnam Massif, Korea. Based on the Ce and Nd isotopic data, we also discuss the REE geochemistry of source material of the Jirisan felsic granulite. The felsic granulite shows three different types of chondrite-normalized REE pattern: one is a tetrad REE pattern of M-type with a large negative Eu anomaly, another is a W-type tetrad REE pattern, and the third is an REE pattern of crustal type showing an LREE-enriched and HREE-depleted pattern. U-Pb zircon and Rb-Sr whole rock ages are 1874 Ma and 1831±36 Ma (2σ) with initial 0.7028±0.0097, respectively. However, Sm-Nd isotopic system from these rocks shows error-chron ages from 1235 Ma to 1570 Ma suggesting that Sm-Nd isotopic system might have been disturbed by specific geochemical processes related to the formation of the tetrad REE patterns. Nevertheless, initial Ce-Nd isotopic values show that all three types were derived from the isotopically similar source materials. Our data also indicate that La-Ce and Sm-Nd isotopic system may be useful in understanding REE fractionation between rock and its source material.
Direct observation of chemical modification of Asian Dust particles during long-range transport

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In our previous works [1-3], it was clearly demonstrated that the combined use of quantitative energy-dispersive electron probe X-ray microanalysis (ED-EPMA), known as low-Z particle EPMA, and attenuated total reflectance FT-IR (ATR-FT-IR) imaging technique had the great potential for detailed characterization of individual aerosol particles. In this work, individual Asian Dust particles collected during an Asian dust storm event occurred on Nov. 11, 2002 in Korea were characterized by the combined use of low-Z particle EPMA and ATR-FT-IR imaging technique. By the combined use of the two single-particle analytical techniques on the same individual particles, it was observed that Asian Dust particles had experienced extensive chemical modification during long-range transport, through heterogeneous reactions with nitrogen or sulfur oxide species resulting in nitrate and/or sulfate formations, respectively. On the basis of information on their morphology, elemental concentrations, and functional groups of individual particles available from the two analytical techniques, overall 109 individual particles were classified into four particle types: Ca-containing (38%); NaNO₃-containing (30%); silicate (23%); and miscellaneous particles (9%). Among overall 41 Ca-containing particles, the numbers of particles containing nitrate, sulfate, and both are 14, 8, and 17, respectively, whereas the number of unreacted CaCO₃ particles is just 2, clearly demonstrating that the Asian Dust particles had extensively experienced heterogeneous reactions during long-range transport. The combined use of the two single particle analytical techniques could provide detailed information on their physicochemical characteristics of individual Asian Dust particles, and thus the identification of airborne amorphous phase calcium carbonate particles and nitrite species in aerosol phase, and mineralogy of silicate particles on a single particle basis could be performed.


The gully nitrogen migration and flux at northern China city

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Research Object and Results
Yitong River at a representative northern China city, Changchun, was selected as research object. We quantitatively investigated the migration path and flux of nitrogen at gully region in the city under rapid urbanization process. The results showed that at Yitong River basin, the total nitrogen input flux was 188 kg/hm², following the sequence of fertilizer input> biological immobilization> feed> atmospheric deposition. The total nitrogen output flux was 102.5kg/hm², following the sequence of products> waste output> denitrification> surface runoff, the net nitrogen storage was 85.5kg/hm². The migration path and flux of nitrogen were obviously by human activities, showing an imbalance of input and output and a tendency of nitrogen accumulation and pollution.

Discussion of Results
Nitrogen migration is a combined effect from meteorology, hydrology, topography and agricultural practices, among which rainfall is the key driving force [1]. The material input and migration directly impact nutrient loss [2]. Under the background of globalization, the nitrogen migration and the biogeochemical processes become extremely complex due to the coupling effects from interfering and natural factors [3], the knowledge about nitrogen source and destination is still very limited, China is localized at monsoon area, where the highest rate of environmental change occurs. Thus, long-term monitoring and modeling regarding entire watershed ecosystem as a whole and quantitative analysis of the coupling mechanism of human activity and natural processes are required. This will provide theoretical support for the healthy evolution and development of cities.

Mechanisms of Cd sorption to montmorillonite (Na-SWy-2) clay affected by ionic strength and microbial ligand

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Many microorganisms exude low molecular weight organic ligands known as siderophores to acquire nutrient Fe; these ligands may also affect the fate and transport of other metals. In this study, we investigated the effects of pH, ionic strength, and the siderophore desferrioxamine B (DFOB) on Cd sorption to montmorillonite using batch experiments, Extended X-ray Absorption Fine Structure (EXAFS) analysis, and X-ray Diffraction (XRD) measurements to monitor changes in montmorillonite 001 d-spacing upon sorption. The extent of Cd sorption to montmorillonite increased with increasing pH and decreasing ionic strength. The presence of DFOB inhibited Cd sorption at pH < ~7 and enhanced Cd sorption at pH > ~7. Sorption densities ranged from 1.1 (11% sorption) to 10.0 (100% sorption) µmol sorbed/gram of clay. EXAFS analysis showed that the detailed sorption mechanism varied as a function of pH, ionic strength and DFOB concentration (0 or 1.0 mM). In the absence of DFOB, at low pH (~5.0 for samples in 0.1M NaNO3 and ~5.0 and ~7.5 for samples in 0.01M NaNO3), EXAFS showed that Cd sorbed outer-spherically; at higher pH (~7.5 and ~8.5 for samples in 0.1M NaNO3 and 8.5 for samples in 0.01M NaNO3), Cd sorbed as a mixture of inner-sphere and outer-sphere complexes. In the presence of DFOB, at pH ~5.0, Cd sorbed outer-spherically; at pH ~7.5 and 8.5, Cd sorbed as a mixture of inner-sphere and outer-sphere Cd-DFOB complexes. Furthermore, the ratio between inner-sphere and outer-sphere sorption increased with both pH and ionic strength. XRD measurements indicate that layer spacing did not vary substantially as a function of Cd concentration, ionic strength, or pH. However, in the presence of DFOB, the d-spacing expanded by ~ 2Å, which is consistent DFOB absorption. This study demonstrates that Cd sorption to swelling clay can involve a complex interplay of mechanisms depending upon environmental conditions.

Experimental fluid-rock interaction simulating brine reinjection in greywacke-hosted reservoirs of the Taupo Volcanic Zone, New Zealand

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A high temperature-pressure fluid-rock interaction apparatus has been used to simulate greywacke - brine interaction at 154°C and 27 bars using a continuously-flowing fluid. The experiment was designed to reproduce the scenario where reinjection brine is disposed in a fractured greywacke aquifer; a typical lithology at New Zealand geothermal power plants. The fluid used was an actual reinjection brine from an operating plant, containing ~3400 mg/kg of total dissolved solids including SiO2 (960 mg/kg), Na (799 mg/kg), K (131 mg/kg), Cl (1027 mg/kg) and SO4 (423 mg/kg). In order to remove atmospheric oxygen contamination, the fluid was degassed first with ultrapure N2 followed by a H2S:N2 mixture (1:100) for 20 minutes. The final pH of the fluid was 6.8 at room temperature. For the simulation, 24 g of crushed, seived and ultrasonically-cleaned greywacke (1-2 mm) was placed in the core holder of the flow-through apparatus. At room temperature and 1 ml/hr of brine flow (one week duration), the reacted fluid attained a pH of 7.8 and contained elevated concentrations of Ca and Mg (77 and 6 mg/kg, respectively). After a temperature increase to 154°C, the reacted fluid remained oversaturated with respect to amorphous silica but a loss of 240 mg/kg of SiO2 was observed. Of the other dissolved species: Mg, Ca, Sr, Al, Mn, and Fe showed a significant decrease; while Li, Na, K, As, and the anions showed no measurable change. Variation of flow rate (0.5 ml/hr) showed little change in effluent chemistry suggesting partial equilibrium with some mineral phases. SEM examination of the run products at the entry point of the brine showed a complete overgrowth of amorphous silica on all mineral surfaces. Reacted material at the exit point of the fluid did not show extensive silica overgrowths indicating removal of polymerised silica nanospherules early during water-rock interaction. Partial equilibrium with a secondary phase containing Ca-Mg-Fe suggests a possible control on fluid composition by calcite and/or clay minerals. This was observed in previous experiments using distilled water. These results show that the silica phase precipitating at these conditions in the geothermal aquifer is amorphous silica.
**Geochemoal fingerprint of an Oligocene to Miocene arc segment in Eastern Mindanao (Philippines)**

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The Oligocene to Miocene arc segment in central Eastern Mindanao (Philippines) is part of the Philippine Mobile Belt (PMB) and is related to the low sulfidation epithermal Co-O mine. The PMB consists of the Paleogene volcanic Philippine arc and accreted crustal fragments from the Eurasian plate [1]. This study of the Co-O magma suite addresses the geochemoal fingerprint of this arc segment, incuding the nature of the mantle wedge, involvement of subducted material such as sediment or crustal fragments (form the Eurasian plate) and relationships between geoecstnic setting and ore forming processes.

The Co-O magma series displays typical island arc geochemical patterns highlighted by the conjunction of LREE-enrichment with depletion of Nb, Ta and Yt. The igneous rocks are dominantly calc-alkaline magma series (andesites and dacites), with some tholeiitic trends for basaltic rocks. There are no significant enrichment of LILE or LREE when compared to younger Pliocene magmas of the Philippines. Nb contents and Zr/Nb ratios (x-y) of the basalts are comparable to other primitive arc magmas in the Pacific (e.g. Marianas) signifying a MORB-like mantle wedge. Th/Ce values below 0.1, and Th/La ratios similar to the Marianas (that are close to mantle values), rule out sediment melting or seaamounts on the slab. This magma series involved thin arc crust in an intraoceanic arc setting related to a potentially intermediate to geothectenic remige, without addition of rifted fragments or slab. This magma series involved thin arc crust in an mantle values), rule out sediment melting or seaamounts on the slab.

**Origin of nepheline-normative primitive magmas in island arcs**

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Here we address the question of the origin of Si-undersaturated arc magmas, although they are rarely emitted on Earth surface, through a systematic on major and trace elements in primitive olivine-hosted melt inclusions. Samples are Mg-rich basalt to ankaramite lavas and lapilli scoriae from different volcanic arcs (Vanuatu, Lesser Antilles, Indonesian, Luzon and Aeolian arcs).

Melt inclusions display trace element patterns typical of arc-related calc-alkaline basalts, with variable enrichments in LILE, Sc (20 to 90 ppm), and La/Yb or Nb/Y ratios ranging from 1 to 18, and from 0.1 to 0.3, respectively. In CMAS projections, the melt inclusions delineate a trend linking two well-defined end-members strongly or poorly enriched in diopside component.

As a whole, the melt inclusions provide snapshots of instantaneous melts recording a compositional diversity of primitive magma batches, which requires the multi-stage mixing between melts generated by partial melting of peridotite and amphibole-bearing clinopyroxene-rich lithologies. This hypothesis is also supported by trace element models including Sc and incompatible element ratios, where melt inclusions form mixing trend between the two lithologies. We conclude that amphibole-bearing clinopyroxenite, occurring as metasomatic segments in the upper mantle of island arcs [1, 2], could be a suitable source for Ne-normative, Di-rich melt inclusions found in arc environments [3-7]. The progressive melting of these lithologies and surrounding peridotite could account for the geochemical characteristics of the studied melt inclusions.

Ni speciation and isotope fractionation in marine ferromanganese deposits

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Marine ferromanganese deposits have slow deposition rates and laminar growth habits. Variations in major and trace element speciation and isotopic composition of successive layers within the crusts have the potential to retain information regarding ocean chemical conditions. It is thought that Ni can incorporated into the structure of marine ferromanganese deposits such that the Ni is retained over time [1],[2]. The goal of this study is to explore Ni isotope systematics in marine ferromanganese deposits as a tracer for metal sources and chemical conditions at the time of Ni sorption.

Our study pairs stable isotopic fractionation measurements (via MC-ICP-MS [3]) with synchrotron X-ray spectroscopy techniques to identify the local coordination environment of sorbed Ni. This is accomplished by using laboratory generated 2-line ferrihydrite, goethite, and hexagonal-birnessite that have had Ni sorbed under a suite of pH values and Ni concentrations. We’re also investigating a range of natural marine deposits such as ferromanganese nodules and crusts from different oceanic basins.

Preliminary findings show that: (1) initial aqueous Ni rates and laminar growth habits. Variations in major and trace element speciation and isotopic composition of successive layers within the crusts have the potential to retain information regarding ocean chemical conditions. It is thought that Ni can incorporated into the structure of marine ferromanganese deposits such that the Ni is retained over time [1],[2]. The goal of this study is to explore Ni isotope systematics in marine ferromanganese deposits as a tracer for metal sources and chemical conditions at the time of Ni sorption.

Preliminary findings show that: (1) initial aqueous Ni concentrations can affect the fractionation of sorbed isotopes, and (2) pH can influence both the structural location of Ni sorption as well as the fractionation of Ni isotopes. Mineral surface charge and structural properties likely control the extent of Ni isotope fractionation. We hypothesize that in a natural deposits, mineralogy together with Ni sources and enrichment conditions are important parameters controlling Ni isotope signatures.


Early Paleozoic granites in the Jiamusi terrane of the Central Asian fold belt

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In the structure of the eastern part of the Central-Asian fold belt a series of continental blocks (terranes) is distinguished. These are: the Argun, Mamyn, Bureya, Jiamusi blocks (terranes) composed of granitoids of different ages but their age has being remained disputable for quite a long time. At present a series of age datings are obtained (U-Pb method). Basing on that datings we can say with certainty that the Early Paleozoic granitoids are widely developed in this terrane.

In the northeastern part of the Jiamusi terrane we obtained the age of 480±4 Ma granites of Sutara massif, the age of 471±10 Ma of leucogranites of the Kabala massif and the age of 461±5 Ma of quartz syenites of the Durilovsky massif.

Similar age values are also given for granites in the south Jiamusi terrane [1] and for granites in the Argun, Mamyn, Bureya terranes [2-5]. In this connection it cannot be excluded that all above mentioned Early Paleozoic granitoids belong to a single orogenic belt.

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Geochemical features of the Amur River sediments in its middle reaches

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The Amur River is one of the largest rivers of the East Asia. The main channel and tributaries of the Amur River cross the geological units of different ages.

A distribution of rare earth elements in the studied samples of the bottom sediments of the Amur River is moderately differentiated ([La/Yb] n=9.6-14.9). A characteristic feature of their distribution is also an enrichment in LREE relatively to MREE and comparatively gentle graph in the in the field of MREE and heavy HREE which is supported by the ratios of [La/Sm]=3.3.- 4.1 and [Gd/Yb]=1.1-2.2. All spectra of rare earth elements have moderately expressed negative Eu anomaly (Eu/Eu*=0.7 -0.9) (Fig.1).

In comparison with the composition of the upper continental crust the bottom sediments under study are at a definite degree depleted in such elements as Sc (3.7 – 9.0 ppm), Cu (8-22ppm), Nb (9-13 ppm), Ta (0.21-0.37 ppm), Y (9-17 ppm). The concentration of Zn (50-75 ppm), Rb (82-109 ppm), Sr (290-350 ppm), Pb (15-24 ppm), W (1.1-2.2 ppm), Th (5.2-11.9 ppm), U (1.0-5.4 ppm), REE correspond to the level of those in the upper continental crust while the concentrations of Ba (550-840 ppm), V (63 – 81 ppm), Cr (63-80 ppm), Co (12-14 ppm), Ni (31-43 ppm), Zr (190-309 ppm) a bit higher than their crust values.

It was established that the most probable sources of the bottom sediments in the studied section of the Amur River were siliceous acid magmatic or metasedimentary rocks.


Systematic underestimation of the oxidation state of MORB glasses

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The Fe3+/Fe of a magma and its fO2 are related by:

$$\frac{Fe^{3+}}{Fe^{2+}} + 0.25 O_2 = \frac{Fe^{3+}}{Fe^{2+}}O_{1.5}$$

This dependence has been calibrated using a wide range of silicate melt compositions equilibrated at known fO2 and analysed by wet chemistry ([1], [2]) and Mössbauer. Analyses of large sets of natural MORB glasses by wet chemistry (e.g. [3], [4]) report tight distributions around Fe3+/Fe2+ ≈ 0.1, corresponding to the relative oxidation state ΔQFM ≈ -0.5. However, recent determinations of Fe3+/Fe2+ on MORB glasses by XANES ([5], [6]) consistently return more oxidised values, about 0.16, corresponding to ΔQFM ≈ +0.5.

The wet chemistry method [7] relies on the complete oxidation of Fe2+ to Fe3+ by reduction of V5+ to V4+. However, it does not discriminate between Fe2+ and other reduced species. One such species, S2-, is present in MORB glasses at ~ 10^3 ppm, but not in the glasses used to establish the Fe3+/Fe2+-fO2 relationship.

To test the effect of S2- during wet chemistry, a series of Fe-free glasses with the An- Di eutectic composition were prepared using CO2-CO-SO2 gas mixtures to produce S2- ranging from 0 to 4500 ppm [8]. These glasses were subjected to the procedure of ref. [7]. The results establish that S2- is fully oxidised during dissolution to S6+ (i.e. sulfate) according to the reaction:

$$S_2^- + 8V_5^+ = 8V_4^+ + S_{6^+}^-$$

From the reaction stoichiometry, 1000 ppm S2- is equal to 2 wt% Fe2O3, which is more than enough to account for the discrepancy in the Fe3+/Fe2+ of MORB between wet chemistry and XANES. Determination of S and its speciation in basalts is essential to understanding their redox state, since degassing of S as SO2 will tend to further reduce basalts with S2- but oxidise basalts with S6+ [9].

Searching for ancient crusts: Integrating Pb isotopes in plagioclase with Hf isotopes in zircon

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The composition of the Earth’s early crust is a topic of much interest in geology today. We present in situ analyses by LA-MC-ICPMS for the Pb isotope compositions of preserved igneous plagioclase (An 75-89) megacrysts and the Hf isotope compositions of BSE-imaged domains of zircon grains from 21 samples from two anorthosite complexes in southwestern Greenland, Fiskenæsset and Nunataarsuk, which represent two of the best-preserved Archean anorthosites in the world. In situ LA-ICPMS U-Pb geochronology of the zircon grains suggests that the crystallization age of the Fiskenæsset complex is 2936 ± 13 Ma (2σ, MSWD = 1.5) and the Nunataarsuk complex is 2914 ± 6.9 Ma (2σ, MSWD = 2.0). Initial Hf isotope compositions of zircon grains from both anorthosite complexes fall between depleted mantle and a less radiogenic crustal source with a total range up to 5 *Hf units. In terms of Pb isotope compositions of plagioclase, both anorthosite complexes share a depleted mantle end member yet their Pb isotope compositions diverge in opposite directions from this point: Fiskenæsset toward a high-µ, more radiogenic Pb crustal composition and Nunataarsuk toward low-µ, less radiogenic Pb, crustal composition. By using Hf isotopes in zircon in conjunction with Pb isotopes in plagioclase we are able to constrain both the timing of mantle extraction of the crustal end member and its composition. At Fiskenæsset, the depleted mantle melt interacted with an Eoarchean (~ 3600 – 3800 Ma) mafic crust with 176Lu/177Hf ~ 0.026. At Nunataarsuk, the depleted mantle melt interacted with a Hadean (~ 4200 Ma) mafic crust with 176Lu/177Hf ~ 0.032. Using our new in situ approach, contamination of mantle derived magma by ancient mafic crust has been discovered in both the Fiskenæsset and Nunataarsuk anorthosite complexes of Greenland. The isotope data presented here suggest the survival of Hadean and Eoarchean crust until ~ 2900 Ma. There is potential that this old mafic crustal could be preserved at the surface within the Nunataarsuk and Fiskenæsset regions today.

REE and isotope (Sr, S, Pb) geochemistries to constrain the genesis of the F-(Ba-Pb-Zn) ores of the Zaghouan District (NE Tunisia)

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The F-(Ba-Pb-Zn) ore deposits of the Zaghouan District, which are located in NE Tunisia, occur as open space fillings or stratabound orebodies, hosted in Jurassic, Cretaceous and Tertiary layers. Ore fluids are hydrothermal (80 to 200°C) brines (10 to 30 wt % NaCl equiv.). The chondrite-normalized REE patterns may be split into three groups: (i) ‘Normal marine’ patterns characterizing the wallrock carbonates; (ii) REE patterns sloping to the right-hand side, with small negative Ce and Eu anomalies, characteristic of the early ore stages; (iii) Bell-shaped REE patterns displaying LREE depletion, as well as weak negative Ce and Eu anomalies, characterizing fluids of subsequent stages. The 87Sr/86Sr ratios, show that the Sr of the epigenetic carbonates (dolomite, calcite) and ore minerals (fluorite, celestite) is more radiogenic than that of the country rocks. The uniformity of this ratio throughout the District, provides evidence for the isotopic homogeneity and, consequently, the identity of the source of the mineralizing fluids. The δ34S values of barite associated to mineralizations, are close to the δ34S of Triassic sea water (17%). The δ34S values of sulphide minerals show a wide range for galena (-13.6 to +11.4%), but restricted for sphalerite (-2.6 to +2.1%). However, considered individually, each deposit is characterized by a restricted range of δ34S values for both sulphides, which requires that reduction took place in closed systems. The more negative δ34S values are assigned to bacterial reduction, while the more positive are assigned to thermo-chemical reduction of Triassic sulphates. Taking account of the homogeneity in the Pb-isotope composition of galenas, a single upper crustal source for base-metals is accepted. The Late Paleozoic basement seems to be the more plausible source for F-Pb-Zn concentrated in the deposits. The formation of the Zaghouan District ore deposits is considered as the result of the Zaghouan Fault reactivation during the Upper Miocene period.
Binge/purge oscillations of the thawing Fennoscandian Ice Sheet revealed by \(\varepsilon_{\text{Nd}}\) and biomarkers

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At its maximum extent, the FIS advanced into the watershed of the Dnepr River, one of the main rivers feeding the former Black Sea ‘Lake’. As a consequence, the Black Sea basin potentially represents a suitable location to investigate the dynamics of the FIS retreat and its impacts on global/regional climate and European hydrographical reorganizations in the context of the Last Deglaciation.

Here, we report high-resolution geochemical data from a core retrieved in the Black Sea. We combine the use of Nd isotopes in clay fraction (\(\varepsilon_{\text{Nd}}\)) and bulk XRF-Ti/Ca as tracers for sediment provenance, together with biomarkers as tracers for river runoff (BIT-index) and boreal soil leaching (C\(_{25}\)-alkanes). During Heinrich Event 1 (HE1), four drastic periods of Deglacial Water Pulses (DWPs) occurred as unequivocally revealed by the biomarkers. Concomitantly, \(\varepsilon_{\text{Nd}}\) signatures clearly demonstrated that the DWPs were generated by the thawing FIS. Each period of DWPs (~200 yr in duration) occurred repeatedly every 200 yr, displaying a peculiar cyclic-like pattern. By analogy with MacAyeal [1]’s model, we propose a binge-purge model to explain the observed cyclicity: the binging period requiring a continuous FIS retreat, the purging period involving regional interactions between the formed proglacial lakes and the atmosphere.


Impact of aerosols on the equilibrium response of the climate system

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Aerosols have both a direct and indirect effect on climate. The first effect arises from the aerosol scattering and absorption of radiation in the atmosphere. The indirect effect relates to their influence on cloud properties.

In the present study, we investigate the equilibrium response of the climate system to two scenarios of primary emissions of black carbon, organic carbon, sulfur dioxide, benzene, toluene, and xylene correspondent to 1850s and today conditions. We use the fully-unified aerosol-climate model ECHAM5-HAM coupled to a mixed layer ocean (MLO)[1, 2, 3]. Using a MLO coupled to the climate-aerosol model allows us to diagnose the aerosol impact in a comprehensive manner. The emissions were taken from the ACCMIP (Atmospheric Chemistry & Climate Intercomparison Project) [4], an inventory developed for the next IPCC assessment.

We will show results of several equilibrium simulations with a focus on the response of the hydrological cycle to aerosol effects, like impacts on water vapour, sensible heat fluxes, precipitation minus evaporation patterns, convective mass fluxes, etc. Preliminary results indicate that the aerosol forcing of black carbon, organic carbon, and sulfur dioxide from 1850s to present day resulted in a global mean surface cooling of 0.9K, a reduction in global mean precipitation of 0.11mm/d (3.41%), and an increase in cloud cover of 1.1%.

**A 50-year record of PGEs in Antarctic snow**

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Antarctic snow preserves an atmospheric archive that enables the study of global atmospheric changes and anthropogenic disturbances from the past. We report atmospheric deposition rates of platinum group elements (PGEs) in Antarctica during the last ~50 years based on determinations of Pt, Ir and Rh in snow samples collected from Queen Maud Land, East Antarctica to evaluate changes in the global atmospheric budget of these noble metals. The 50-year average PGE concentrations in Antarctic snow were 17 fg g⁻¹ (4.7–76 fg g⁻¹) for Pt, 0.12 fg g⁻¹ (<0.05–0.34 fg g⁻¹) for Ir and 0.71 fg g⁻¹ (0.12–8.8 fg g⁻¹) for Rh. The concentration peaks for Pt, Ir and Rh were observed at depths corresponding to volcanic eruption periods, indicating that PGEs can be used as a good tracer of volcanic activity in the past. A significant increase in concentrations and crustal enrichment factors for Pt and a slight enhancement in enrichment factors for Rh were observed after the 1980s. This suggests that there has been large-scale atmospheric pollution for Pt and probably Rh since the 1980s, which may be attributed to the increasing emissions of these metals from anthropogenic sources such as automobile catalysts and metal production processes.

**Geochemistry and distribution of total heavy mineral concentrations of beach sediments of the Sakarya Delta (SW-Black Sea)**

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This study aims to investigate geochemistry and total heavy mineral distributions of marine beach sediments of the Sakarya Delta (SW-Black Sea, Turkey) where some higher metal contents were reported in sediments and related to possible occurrences of beach placers. With support of TÜBİTAK (Project No: 108Y333) and Ankara University-Sci. Res. Pro. Of. (Project 20070745007HPD), 48 surficial sediment samples were collected from the coastal beaches of Sakarya Delta representing modern shoreline and backshore sub-environments. In addition to geomorphological field observations, multielement and grain size analysis as well as total heavy mineral determinations are performed. Multielement geochemistry was carried out using ICP-MS method. Preliminary results showed that beach bulk sediments of the Sakarya Delta generally contained similar amounts of Ti, Pb, U, Mg and Sn compared with average rock composition of Earth’s crust. The concentrations of As (6-24 ppm), Sb (0, 3-2, 1ppm), Ca (2- 9 ppm), Cr (17-3999 ppm) were comparatively higher whereas Cu (6-27 ppm), Mo (0, 1- 0, 7 ppm), Sn (0, 4-5, 2 ppm), Y (5-27 ppm), Nb (4-36 ppm) and Ta (0, 3-2, 5 ppm) contents are lower. Elements Cr, Fe, Mn, Co, Ni, Nb, Y and Ce reached their highest concentrations in sediments collected close to the Sakarya River mouth. The total heavy mineral concentrations of the bulk sediments are generally low, with except of 3 samples which contained highest total heavy mineral concentrations (70-95 %). The locations of these 3 samples were also aligned to or towards the river mouths.
Recycling elements from the slab to arc crust: Insights from element mass balance of the Izu arc system

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One of the most important processes leading to formation of continental crust is element transfer from subducting lithosphere to newly-formed arc crust. Despite extensive study of HP/UHP metamorphic rocks that represent paleo subducted slabs and experiments to replicate subduction zone conditions, little consensus has been reached on the nature of the mass transfer agents (e.g. aqueous fluid or hydrous melt), or the efficiency of the recycling process. Here, I use a mass balance of K and Ce in the Izu arc system as an alternative approach to resolving recycling processes in subduction zones. Potentiality, it has been shown that these phases in the slab means K and Ce in slab fluids should be buffered to beyond sub-arc depths.

The Izu arc was chosen for this study as the subducting Pacific slab is relatively cold and has been well characterised for chemical composition. The -50 Ma tectonic and magmatic activity of the arc is well constrained, and the volume and composition of the arc crust can be accurately determined thanks to an excellent ash record, numerous seismic profiles of the arc and exposure of mid/lower arc crustal sections in the Tanazawa plutonic complex, Honshu.

Rates of arc crustal growth are calculated to be 130 - 200 km^3 km^-1 strike length m. y.^-1. Comparing the composition of this crust (corrected for mantle input and subduction erosion) to subduction inputs reveals that 50 to 90% of the K and 10 to 15% of the Ce is recycled from the subducting plate back to the arc crust. Using experimentally-determined solubility relations, these fluxes would require all of the available water in the sub-arc crust plus a 0.1 - 0.7 km column of slab serpentinite if the mass transfer agent is a hydrous slab melt. By contrast, excessive volumes of slab serpentinite (6 - 60 km thick column!) are required to provide the water needed if the transport agent is an aqueous fluid. These results confirm slab melts to be the dominant mass transfer agent in the Izu subduction zone and highlights the importance of subducted serpentinite as a water source for arc magmatism.

How to safely store water samples prior to stable hydrogen and oxygen isotope analyses?

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Safe storage of water samples between sampling and their stable hydrogen and oxygen isotope analyses (determination of δ^2H and δ^18O values) is still a topic of concern in hydrological studies. Water sorption and the diffusive transfer of water molecules through organic polymeric material may entail an isotopic fractionation. A methodological study of the variation of δ^2H and δ^18O values of waters stored in different type of bottles was performed.

A set of sixteen bottles of eleven different organic polymers (plastics), including low and high density polyethylene (LDPE and HDPE), polypropylene (PP), polycarbonate (PC, polyethylene terephthalate (PET), and high resistance Teflon® (PFA) from different size (10 to 500 mL) and wall thickness (0.20 to 1.50 mm) were completely filled (no headspace) with the same bottled water coming from a single natural spring (Evian® water, Evia-les-Bains, France) and were properly closed. Additionally, 16 narrow neck bottles of amber glass were filled with the same water for comparison.

Rates of arc crustal growth are calculated to be 130 - 200 km^3 km^-1 strike length m. y.^-1. Comparing the composition of this crust (corrected for mantle input and subduction erosion) to subduction inputs reveals that 50 to 90% of the K and 10 to 15% of the Ce is recycled from the subducting plate back to the arc crust. Using experimentally-determined solubility relations, these fluxes would require all of the available water in the sub-arc crust plus a 0.1 - 0.7 km column of slab serpentinite if the mass transfer agent is a hydrous slab melt. By contrast, excessive volumes of slab serpentinite (6 - 60 km thick column!) are required to provide the water needed if the transport agent is an aqueous fluid. These results confirm slab melts to be the dominant mass transfer agent in the Izu subduction zone and highlights the importance of subducted serpentinite as a water source for arc magmatism.

Particulate Organic Carbon deposition offshore Taiwan following typhoon Morakot

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Woody debris and petrogenic carbon can be exported by hyperpycnal discharge from the fluvial and shallow-marine system, and stored on geological timescales in basins, but offshore storage of fresh Particulate Organic Carbon (POC) and the efficiency of burial of petrogenic carbon are poorly constrained. We present a case from Taiwan, where riverine fluxes are known [1].

Following Typhoon Morakot (2009, up to 3m rainfall), eight sediment cores totalling 191 cm were collected from turbidites in the Kaoping submarine canyon at depths up to 976 m, and from the neighbouring slope. Coarse, modern woody debris was present in 32% of core samples, exclusively within the sandy parts of turbidites. Total Organic Carbon concentrations were highest in slope deposits, averaging 0.59%, and in sandy canyon deposits. Canyon and floodplain samples had similar distributions of isotopic values, suggesting mixing of two endmembers. One is a combination of fresh woody debris and recycled coal-grade material from sedimentary rocks in the hinterland. The other is higher-grade carbonaceous material including graphite, likely from the central mountain belt. The river signal was fully preserved in the canyon. Slope deposits had a lighter $^{13}$C signature indicating marine organic carbon input.

Raman spectroscopy suggests that high-grade graphite and low-grade material were sourced from Plio-Pleistocene deposits in the western foreland, whilst intermediate-grade graphic material was sourced from the central mountain belt. High-grade graphite metamorphic conditions are not exposed in Taiwan: this material must have survived at least two cycles of erosion and deposition.


Time-resolved metal(loid) reactivity at biogeochemical interfaces

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The rates of important chemical processes at biogeochemical interfaces including ion exchange, sorption, and redox can occur over wide time scales. Ex-situ batch and flow techniques offer high elemental sensitivity, but their time resolution is not adequate to capture rapid reaction rates that often comprise a significant portion of many processes such as sorption and oxidation-reduction. Measurement of rapid, initial rates of environmentally important reactions at the mineral/water interface is critical in determining reaction mechanisms. Until recently, experimental techniques with sufficient time resolution and elemental sensitivity to measure initial rates were very limited. Some techniques such as pressure-jump methods can capture rapid reactions on millisecond time scales, but the rate parameters are indirectly measured and reaction mechanisms can only be inferred. Ideally, one would prefer to follow reaction rates in real-time, in situ, and at the molecular scale to definitively determine reaction mechanisms. In this presentation the use of in situ synchrotron-based, quick scanning X-ray absorption spectroscopy (Q-XAS), at sub-second time scales, is applied to measure the initial oxidation of As(III) and Cr(III) by hydrous manganese oxide [1], [2]. Results indicate that with these techniques, chemical kinetics are being measured. The rapid kinetic techniques are coupled with synchrotron-based XAS and XRD, and a stirred-flow technique, to provide a comprehensive assessment of As(III) and Cr(III) oxidation kinetics and mechanisms on hydrous manganese oxide over a range of temporal scales [3], [4].

Rapid age determination of oysters using shell Mg/Ca ratios

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Magnesium to calcium (Mg/Ca) ratios exhibit a strong temperature dependence in foraminifera and corals, but not in bivalve mollusks. Various studies have reported Mg/Ca-temperature relationships with R² values ranging from 0.8 to 0.3, and significantly different relationships for bivalves growing at different salinities was reported. However, this poor temperature correlation does not render Mg/Ca data useless. A weak temperature dependence would allow time (seasons and years) to be determined along the growth axis of shells. This would provide information about age, growth rate and also allow other proxies to be aligned with time. Previous studies have shown that Mg/Ca ratios can indeed by used for this purpose in a gastropod and pen shell (Pinna); these studies hand drilled powders from the shells and analyzed them using wet chemistry, which is relatively time consuming. Line scans using laser ablation systems can cover several centimeters of shell in a few minutes. If line scans could be used to put calendar dates on shell material it would allow very rapid assessment of the aforementioned variables. We test this method on the resilifer of two oyster species (Crassostrea gigas and C. virginica) using a CETAC LSX-213 laser ablation system coupled to a PE Elan 6000 DRC ICP-MS. Shells of both species exhibit annual cyclicity in Mg/Ca ratios using spot and line scan laser sampling, which matches the seasonal cyclicity determined using stable oxygen isotopes. Elemental maps will be generated to determine the distribution of Mg over the resilifer. Our preliminary results suggest that line scans offer a rapid technique for determining age, growth rate and timing of shell growth in oyster resilifers.

Super-Si garnet breakdown kinetics and implications for craton evolution

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Decompression experiments have shown that super-Si garnet (Grt) decomposes to Grt + pyroxene (Pyx) with specific micro-structures [1, 2]. They support that natural analogues (found in mantle xenoliths, diamond inclusions, massif peridotites) record up to several hundreds of kilometre exhumation - all believed to apply to contrasting geological scenarios including mantle convection, kimberlite magmatism and plate tectonics [2-4].

Here we used glass powder with a ‘pyrolite minus olivine’ composition for polycrystalline dry super-Si Grt synthesis (18 GPa, 1600 °C, 2.3 h) and subsequent decompression (10 GPa, 1450 °C, 0-12 h). All recovered samples have a granular coronitic texture of new Grt+Pyx surrounding relic super-Si Grt cores. Quantified XRD spectra show transformed volumes are similar, ~40%. The mineral chemistry (EDS) of breakdown products differs from that of corresponding equilibrium minerals synthesised along with each decompression experiment. In contrast, most natural analogues are chemically equilibrated requiring that volume diffusion exceeded initial breakdown. Modelling of Si-Al interdiffusion in Grt suggests that grains below 10 µm in size or lamellae spacing are able to chemically equilibrate at temperature-time conditions corresponding to those of both kimberlite eruption and ultra-high pressure metamorphism at convergent plate margins. Larger sizes and spacings require upper mantle residence for equilibration.

Results show that super-Si Grt transformation during decompression occurred partially and within the first minutes, but barely continued during the experiments. By implication, natural analogues record a multi stage process: fast decomposition during decompression (corona formation) before volume diffusion (chemical equilibration and lamellae formation) during sub-continental lithospheric mantle (SCLM) residence before final exhumation to the Earth's surface by different geological processes. Given the affinity of super-Si Grt breakdown microstructure occurrence to Archaean areas at global scale, models for craton stabilisation demand the inclusion of processes suitable for: (1) cargo through the upper mantle, like mantle convection/plumes, and (2) SCLM growth in the Grt-peridotite stability field. Shallower stages would have erased the microstructural record.
Zircon from kimberlites of the Nyurbinskaya pipe as indicator of kimberlite emplacement and lithosphere evolution

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About 300 zircon grains have been recovered from the kimberlite concentrate of the Nyurbinskaya pipe with the aim of finding mantle zircons that would allow estimation of the age of kimberlite emplacement. We evaluated the kimberlitic or crustal origin of individual zircon grains using a two-step approach. The first step included the preparation of mounts, collecting cathodoluminescence images of the zircons, electron microprobe analysis of major elements and LAM-ICPMS analysis of trace elements. These data identified zircons with low content of U (<50ppm) and Y (1-150ppm) and low Nb/Ta (<3) ratio of probable mantle (kimberlitic) origin and zircons of crustal origin with increased Y and U content.

The second step involved U-Pb dating and Hf-isotope analysis. The largest population, consisting of crustally-derived zircons, defines a U-Pb age peak at ca 2700 Ma, probably representing the Archean age of the lower crust below the Nakynsky kimberlite. This main population shows a range of εHf (t) values of 3.2 to -14.6 and TDM crustal model ages between 3.6 and 2.7 Ga, and suggests that at least 70% of the deep crust was formed from 3.2-2.8 Ga ago. The minor age population represented by the kimberlite zircons of the Nurbinskaya pipe gave a weighted mean 206Pb/238U age of 381±7 Ma, which is considered as the best estimate for the kimberlite emplacement. The zircons of this younger age population have a narrow range of εHf(t) values of -33.5 to -34.5 and TDM crustal model age of 3.2 Ga.

Are aliphatic monomers of grasses and herbs useful biomarkers for vegetation shifts?

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Each plant species has a unique aliphatic composition. The aliphatic monomer composition of different grasses and herbs was analyzed to investigate whether the pattern can be traced back after decay and transformation into soil organic matter (SOM).

We analyzed the aliphatic monomer pattern (e.g. Alkanols, Alkanoic acids, Alkanes) of dominant grasses and herbs as well as of soil samples derived from four different regions where recently vegetation shifts took place or are assumed to have taken place (Bayerischer Wald and Limestone Alps, Germany; Bagé, Brazil; Qinghai, Tibet). Our aim was to develop a robust classification model for SOM source and vegetation history using these biomarkers. The data on the composition of the aliphatic monomers of the grasses and herbs were analyzed with three different classification models (linear, non-linear and binary), to find the best model to classify the different plant species. Based on the discriminant equations obtained, soil samples were classified and the performances of the three classification models were compared.

We yielded a series of monomers corresponding to previously reported hydrolysates [1, 2, 3], that discriminated significantly among the different grass and herb species. Hence, all tested classification models discriminated sufficiently among the grass and herb species. Between 56% and 85% of the cases were classified correctly, depending on the respective site, the training set and the used model. However, the aliphatic pattern in soils is subjected to changes during decomposition of the plant material and the different biomarker monomers exhibited different turnover rates. Thus, only a multivariate binary classification model that did not rely on quantitative properties and compound ratios was sufficient to classify in average 67% of the soil samples correctly, depending on their decomposition status.

Rates of crystal nucleation and growth from inversion of natural crystal size distributions

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Magmatic textures provide sensitive record of physical processes and variables during magma solidification. Quantitative characterization of texture is thus a useful tool for interpreting the thermal regime and rates of crystal nucleation and growth. Here we show that different pairs of nucleation and growth rate functions can result in textures having identical crystal size distributions (CSD). In order to eliminate such ambiguity of CSDs, we use time variation in crystallinity as an additional constraint leading to unique nucleation and growth rates. While the nucleation rate strongly depends on the CSD slope, curvature and fluctuations, the character of growth rate curve is more related to changes in crystallinity. When crystallinity increases quasi-linearly with time, the growth rate diverges to very high values at the beginning and the end of crystallization, due to small area of solid-liquid interface. That is, the growth rate is lowest at moderate crystallinities, when the crystal surface area is largest. This transient behavior also facilitates approach to equilibrium. When we employ relevant thermal cooling model and bracket the total crystallization by liquidus and solidus temperatures, we can estimate the total crystallization time, and scale all rate functions into real units. Estimated rates of crystal growth are inversely proportional to magma chamber size, and increase non-linearly from its interior to the margin. Application to solidification time and CSDs of the Hawaiian lava lakes results in growth rates of about $10^{-11}$ cm s$^{-1}$, which is in good agreement with natural observations. The growth rates can be converted to crystallization time for any grain size of interest. In log-linear CSDs, the growth time of the most abundant grain size varies from $\sim 1/10$ of the characteristic cooling time for crystals in the pluton interior to $\sim 1/400$ for those near the contacts. Relative growth times thus depend on neither a CSD slope nor a magma body size. The changes in crystal size with time allow us to predict the distance of movement due to action of gravitational forces. The crystal travel distance increases quadratically with the magma chamber size, rendering the crystal settling to be most efficient in large reservoirs. For kilometer-sized bodies we predict that a crystal moves across half of a magma chamber even in viscous magmas, up to 10$^6$ Pa. s.

Stability and breakdown of Ca$^{13}$CO$_3$ melt combined with formation of $^{13}$C -diamond in static experiments up to 80 GPa and 4000 K

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PT conditions of Ca$^{13}$CO$_3$, melting, stability of the melts, and their decomposition by the reaction Ca$^{13}$CO$_3$ = CaO + $^{13}$CO$_2$ (fluid) are investigated at static pressures of 8.5 – 80.0 GPa and temperatures of 1900 – 4000 K with the use of diamond anvil cell and laser heating. The occurrence of $^{13}$CO$_2$ is accompanied by formation of $^{13}$C-diamond (above 11 GPa) and $^{13}$C-graphite (below 11 GPa) that is indicative for the $^{13}$CO$_2$ breakdown to $^{13}$C and O$_2$. Another ‘solution-melt’ mechanism of isotope-pure $^{13}$C-diamond synthesis was realized in melts of the carbonate Ca$^{13}$CO$_3$ - $^{13}$C-graphite (metastable phase) system in the multianvil press at pressures 8.5 and 20 GPa and temperatures up to 2500 K. It was first found in static high pressure experiment that melting of Ca carbonate is congruent over a wide 11.0 – 80.0 GPa pressure interval at temperatures up to 3400 K. It is also important that the phase region for the Ca carbonate melts is sufficiently wide extending from 2300 to 3500 - 3800 K at the 20.0 – 80.0 pressure range. Of particular interest is the first experimental evidence for diamond formation in the two-phase region CaO + CO$_2$ (fluid). The use of isotope-distinguished carbonate Ca$^{13}$CO$_3$ in the diamond anvil cell experiments gives an unambiguous evidence that $^{13}$C-diamond has been formed from Ca$^{13}$CO$_3$ melt by a two-stage decomposition reaction: (1) Ca$^{13}$CO$_3$ (melt) = CaO + $^{13}$CO$_2$ (fluid) and (2) $^{13}$CO$_2$ (fluid) = $^{13}$C (diamond) + O$_2$.

The results are applied to the construction of PT phase diagram for the CaCO$_3$ join (of the CaO – C – O$_2$ system) up to 80 GPa and 4000 K. The melting and decomposition relations of the CaCO$_3$ join as well as accompanying processes of diamond formation are applied and discussed in the context of the problem of natural ‘super deep’ diamonds origin in carbonate-rich growth media of the transition zone and lower mantle of the Earth.

Aerosol mass spectrometer constraint on the global secondary organic aerosol budget

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The budget of atmospheric secondary organic aerosol (SOA) is very uncertain, with recent estimates suggesting a global source of between 12 and 1820 Tg (SOA) a\(^{-1}\). We used a dataset of aerosol mass spectrometer (AMS) observations and a global chemical transport model to produce top-down constraints on the SOA budget. We treated SOA formation from biogenic (monoterpenes and isoprene), lumped anthropogenic and lumped biomass burning volatile organic compounds (VOCs) and varied the SOA yield from each precursor source to produce the best overall match between model and observations. Organic aerosol observations from the IMPROVE network were used as an independent check of our optimised sources. The optimised model has a global SOA source of 140 ± 90 Tg (SOA) a\(^{-1}\) comprised of 13 ± 8 Tg (SOA) a\(^{-1}\) from biogenic, 100 ± 60 Tg (SOA) a\(^{-1}\) from anthropogenically controlled SOA, 23 ± 15 Tg (SOA) a\(^{-1}\) from conversion of primary organic aerosol (mostly from biomass burning) to SOA and an additional 3 ± 3 Tg (SOA) a\(^{-1}\) from biomass burning VOCs. We used a dataset of 14C observations from rural locations to estimate that 10% of our anthropogenically controlled SOA is of urban/industrial origin, with 90 Tg (SOA) a\(^{-1}\) (90%) most likely due to an anthropogenic pollution enhancement of SOA from biogenic VOCs.

Differentiation of impact-melt sheets: Evidence from Manicouagan with implications for the Moon

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Introduction

Recent exploration drilling of the late Triassic, ~80-90 km rim-diameter Manicouagan impact structure, Canada, has yielded ~18 km of core from 38 locations, three holes of which are >1.5 km deep [1]. This new data provides unprecedented insight into the internal structure and composition of a relatively large crater. Complemented by an ongoing 10-year (2006-2016) ground-based research project (the Manicouagan Impact Research Program: MIRP), the goal is to better understand impact crater tectonics and the formation and evolution of impact melt bodies. This is being achieved through training undergraduate, MSc and PhD students, in collaboration with PDFs and Research Scientists, as well as colleagues working internationally.

Impact melt characteristics – new revelations

The drilling program has revealed that the Manicouagan impact melt sheet is not of uniform thickness (previously considered ~300 m thick), but includes considerably thicker sections: up to ~1000 m of clast-poor impact melt, underlain by ~400 m of clast-rich impact melt [2]. These thicker sections of melt comprise a monzodioritic Lower Zone (~500 m), a quartz monzodioritic Middle Zone (~250 m) and a quartz monzonite Upper Zone (~275 m). This is only the second impact structure known to unequivocally exhibit differentiation (previously, Sudbury was the sole exemplar). Geochemical investigation of the thicker melt sheet sections indicates that they formed via fractional crystallization [2].

Impact melt sheet-footwall relations

Drilling results, coupled with field work, have revealed that the interface between the impact-melt sheet and footwall is not flat, but exhibits more complex ‘topography’, which strongly implicates the presence of fault-controlled structure [3]. This new evidence allows the construction of hypothetical cross-sections, which provide insight into central peak and terrace collapse formation mechanisms for complex craters on Earth, the Moon, Mars and beyond.

On modeling H\(^+\) and U transport behavior in an acidic plume

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A nearly 1 km long acidic plume has developed under the F-Area at the U.S. Department of Energy Savannah River Site, South Carolina, from the disposal of low-level acidic radioactive waste solutions into seepage basins overlying relatively permeable, mostly sandy sediments. The disposal operations lasted for about 35 years until 1990, when the seepage basins were solidified and capped. Since then, the groundwater pH in the plume has remained mostly in the 3–3.5 range despite the end of disposal operations and fast groundwater velocities, although U concentration adjacent to the basins has been decreasing exponentially.

Here, we report on exploratory geochemical and reactive transport modeling investigations conducted to assess the relative roles of surface protonation and mineral precipitation in slowing down the rebound of pH at this site, as well as U transport behavior downgradient of the disposal basins. The modeling work is integrated with investigations of ‘reactive facies’, which aim at identifying specific types of sediments with unique properties affecting reactive transport, then correlating these sediment types with lithologic facies and their associated geophysical signatures for estimation of reactive properties over plume scales.

One- and two-dimensional reactive transport simulations were conducted considering Al and Fe mineral dissolution and precipitation, as well as H\(^+\) and U surface complexation models from the literature. Simulations indicate that H\(^+\) sorption reactions on goethite and kaolinite (primary minerals at the site besides quartz) could buffer pH at the site for long periods of time. The precipitation of Al silicates, hydroxides, and/or hydroxy sulfates could also strongly impede pH rebound at the site. Although the pH is computed to rebound quite slowly, U concentrations could potentially decrease at comparatively much faster rates from dilution with clean recharge water. Simulations results are most sensitive to reactive surface areas, to relative rates of reaction versus acidic discharge, to relative rates of mineral precipitation and dissolution, and to the type of implemented sorption models and parameters. The model sensitivity to heterogeneous fields of permeability and reactive surface areas derived from the reactive facies investigations is also investigated.

Biomineralization and growth mechanism of morphologically controlled strontium carbonate

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Biomineralization is a growing discipline in modern earth science and is attracting much attention as it helps us (i) to synthesis marine carbonates with required morphology, composition and structure and (ii) to understand and quantify the controlling factors which affects the microbial mineralization in deep marine environments.[1, 2] The biological systems are very effective at controlling crystal growth, especially polymers have been successfully developed to control crystallization of inorganic particles in aqueous solutions. In this work we report the synthesis of aragonite type strontium carbonate super structures using Gum acacia and also discussed the growth mechanism of the carbonates.

Gum acacia is a branched polysaccharide containing carbohydrates, amino acids, gulcuronic acid and a glycoprotein complex. The functional groups (-OH) present in arabinose and rhamnose and (-COOH) of glucuronic acids play a crucial role in the growth and formation of metal carbonates whereas the proteinaceous core with amino acids (-NH\(_2\)) stabilize the formed metal carbonates and play a key role in mimicking the biomineralization process. The crystallization involves the formation of different hierarchical structures like rice grain, doughnut shaped, flower shaped, hexagonal rods and cross shaped which have never been seen before in natural biominerals. Proteins and polysaccharides with complicated patterns of various functional groups in GA selectively adsorb on to the metal ion thereby hindering the crystal growth, followed by the mesoscale self-assembly of nanometer-scale building block into hierarchical superstructures. The key reaction of CO\(_2\) with Sr\(^{2+}\) ions entrapped within GA polymer leads to the growth of beautiful structures of strontianite. Structural characterization of the synthesized materials was investigated by XRD, SEM, EDAX, TEM, TGA-MS and FT-IR.

Fe and S isotope compositions of hydrothermal sulfides from the Northern Lau Basin

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Massive sulfides belonging to the extinct hydrothermal field of the North Lau Basin were studied for their Fe and S isotope compositions. Sulfide samples belonging to pedestal slab, peripheral chimneys (remnants of white smokers) and oxide precipitates filling the hollows of pillowved basalts were studied. Detailed mineralogical and geochemical studies on the same set of samples indicated the similarities between the Lau hydrothermal field and the Trans-Atlantic Geotraverse (TAG) active mound [1]. The sulfides of pedestal slab mainly consisting chalcopyrites and pyrites with minor barite and sphalerite show δ34S values between 8.4 to 9.6 ‰ (V-CDT). The major constituent of sulfides belonging to peripheral chimney is sphalerite, while pyrite and chalcopyrite being minor. The δ34S values range from 5.5 to 8.3 ‰. These δ34S values are very similar to those of TAG hydrothermal sulfides [2]. Such high δ34S values for TAG hydrothermal sulfides were interpreted as a result of mixing of sulfur of sulfate reduction origin and that of the hydrothermal fluids. The high δ34S values in case of Lau Basin also corroborate the influence of sulfate reduction. The sphalerite-rich sulfides of the peripheral chimney have slightly depleted δ34S values when compared to the pedestal slab indicating increased effect of hydrothermal solutions in them.

The δ56Fe values of samples belonging to pedestal slab show a range between -0.3 to -1.1 ‰ (IRMM-014), while those of the peripheral chimney vary from -0.6 to -1.7 ‰. The oxide precipitates show maximum fractionation in Fe isotope compositions having δ56Fe values of -0.8 and -3.0 ‰. Among the oxide precipitates, the MnO-rich top layer is characterized by lowest δ56Fe value indicating the influence of temperatures. Further, role of redox conditions can be envisaged in controlling Fe isotope compositions based on the correlation between δ56Fe and Ce anomalies.

Mineral growth and dissolution from rare event methods

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Computational theory and hardware have advanced sufficiently to allow in-depth examination of free energy landscapes for complex, geologically important reactions. Here, we used two rare event theories, metadynamics and reactive flux, to probe the attachment and detachment of barium ions to the [120]-oriented monomolecular step on barite and compare these reaction rates and mechanisms to those measured experimentally. This reaction was chosen because attachment and detachment of barium ions to these step-edges is thought to be rate limiting and barite scale has been found to inhibit production of oil and geothermal energy in some cases.

Using metadynamics, we found that detachment and attachment of ions does not occur directly to and from solution, but several intermediate states are observed. Starting from a barium kink site making five bonds to three surface sulfates, detachment first proceeds to a bidentate state containing two bonds to two surface sulfates, followed by an inner-sphere adsorbed species (making one bond), then an outer-sphere adsorbed species before completely dissolving.

Reactive flux calculations of the transitions between each of these states revealed that moving from the inner-sphere adsorbed species to outer-sphere adsorbed is limiting the rate of detachment. For attachment, the transition from inner-sphere adsorbed to the bidentate species is rate limiting. Arrhenius activation energies of each of these rate limiting steps were calculated by performing the reactive flux calculations at multiple temperatures. The activation energies and rate constants, compare favorably to those measured experimentally by atomic force microscopy in the case of dissolution.

The implications this study are two-fold. Firstly, the observation of multiple intermediates states implies that mineral growth and dissolution reactions can lead to pools of labile or recalcitrant material in various states of adsorption onto mineral surfaces. This addresses the longstanding issue of non-steady state dissolution rates. Secondly, the ability to quantitatively probe complex reaction mechanisms on surfaces accurately will be a powerful technique in addressing mineral reactivity and mechanisms.

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A multi-isotope study for identifying groundwater movement near disturbed salt domes: Case study Stassfurt, Germany

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An area of the German part of the Southern Permian basin affected by anthropogenically induced subrosion was investigated for its potential for ongoing salt dissolution induced by groundwater movement. A set of environmental tracers supported by hydrochemical analyses was applied to establish aquifer fingerprints of the covering layers (Quaternary and Triassic) and of flooded parts of the mining area (Zechstein), and revealed prevailing mixing components: A modern groundwater component was identified by the presence of 3H and 3Heu which indicates young apparent groundwater ages (0 - 50 a) in the covering layers. Using this, percentages of modern water could be derived for each sample. The presence or absence of 14C in the samples represents an age classification between the modern groundwater component (<50 a) given above, and an old groundwater component (apparent groundwater ages <50 000 a). The trends derived from radiocarbon could generally be validated by low 4He in samples from the modern groundwater component and elevated 4He in the old groundwater. Contact between meteoric water and Zechstein salts could be identified by the presence or absence of Permian crystallization water from the dissolution of e.g. Carnallite and/or Kieserite in the samples. We developed a conceptual model of groundwater flow and interactions between groundwater of the different aquifers in the studied area and discuss potential implications for ground subsidence.
High-pressure calibration of the oxygen fugacity recorded by garnet bearing peridotites

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The oxygen fugacity within the Earth’s upper mantle below ~50 km depth can be measured by performing oxythermobarometry determinations on garnet bearing mantle xenoliths. The commonly used equilibrium includes the Fe$_3$Fe$_2$Si$_3$O$_{12}$ garnet component. A knowledge of the mantle oxidation state is important in order to understand the speciation of heterovalent elements and C-O-H-bearing volatile-rich phases.

To date, measurements have shown that the upper mantle (>250 km depth) is typically characterized by a heterogeneous $f_O_2$ between -1 to -5 log units relative to the FMQ oxygen buffer. This range mainly arises from the pressure dependence of the employed oxybarometer, which drives the $f_O_2$ to lower values with increasing pressure.

The aim of this study was to investigate the iron oxidation state of garnet equilibrated with carbonate and graphite/diamond in a typical peridotite mantle assemblage in order to test the current oxythermobarometer at high pressure. Experiments were performed using a layer of garnet sandwiched between oxygen buffering carbon/carbonate bearing assemblages, which fixed the oxygen fugacity at known values at pressures between 3 and 7 GPa and temperature of 1100-1600 °C. Several configurations were tested either in the presence of natural Cr-bearing garnets or hydrous conditions and employing both relatively reduced and oxidized starting materials. $f_O_2$ was measured using a sliding redox sensor assemblage employing Fe-Ir alloy. Using these measurements a re-evaluation of the oxythermobarometer calibration was performed. Redox profiles for cratonic mantle were reexamined with implications for carbon speciation in the mantle.

Assessment of carbon needs to renew soil fertility

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Conversion of natural to agricultural ecosystems induces SOM losses due to changes in land management practices and reductions in litter input. The average rate of soil organic carbon (SOC) stock decline after the conversion of a native land to cropland decreases in time [1] and depends on the previous landuse type (forest, grassland, shrubland), and the decomposition regime (determined by climatic conditions, size of the carbon litter input, texture and other factors). SOC can be depleted by 50% in about 5 years in the tropics and 50 years in temperate ecoregions. On the basis of soil resilience and sustainability of agriculture, the adoption of appropriate agricultural practices for the maintenance of carbon in croplands is a win-win situation because they will prevent erosion and contribute to inherent soil and product quality, biodiversity, fertility, water quality, and agricultural economy [2]. Monitoring field data and modeling exercises are essential for the assessment of the turnover of different carbon pools in order to optimize organic input strategies for carbon sequestration in stable forms so as maintain soil structure and fertility [3]. In this work, grassland to cropland and forest to cropland conversions under different climatic regimes were modeled with ROTH-C. Chronosequence literature data for dryland steppes [4], temperate grasslands [5], mediterranean shrublands [6] and forests in the tropics [7] were used for the modeling. The methodological approach for model calibration and estimation of uncertainty presented by Stamati et al. (2011) [4] was followed. Appropriate carbon addition under different climatic regimes and soil textures are suggested for sustainable agricultural practices (carbon sequestration, HUM increase).

Experimental determination of the hydrous basalt liquidus

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A series of experimental liquidus determinations have been carried out on a hydrous primitive basalt at a range of lower crustal pressures. The starting composition replicates the major element chemistry of an olivine picrite from South East Mountain, Grenada, Lesser Antilles with 15.3 wt % MgO and Mg# = 73. The island is known for erupting primary mantle melts, and products of the arc volcanism from Grenada yield evidence for magmatic water contents of +6.4 wt % H2O [1].

The ultimate aim of this experimental series is to map out the topology of the hydrous basalt liquidus. The position of the liquids relative to a mantle adiabat determines the amount of superheating experienced by a magma as it ascends to lower pressures. This in turn has implications for the manner in which mantle-derived melts interact with the crust.

Equilibrium experiments are being conducted using both piston cylinder and TZM apparatus at pressures ≤ 1.7 GPa and water contents of 2.5 and 5.0 wt % at fO2 = NNO. Experiments on the most hydrous starting composition are ongoing and have bracketed the liquidus between temperatures of 1265-1280°C at 1.3 GPa and 1250-1280°C at 1.7 GPa.

These experiments are also being used to explore phase relations at high temperatures and investigate the potential for multiple saturation points. At 1.7 and 1.3 GPa the liquids phases are olivine, clinopyroxene and Cr-rich spinel.

A further objective of this project is to extend the P-T range of experiments in an attempt to recreate the assemblages found in cumulate xenoliths from Grenada.


Effects of diagenesis in Triassic limestone of Opoliske Voivodesip

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Introduction

During Middle Triassic time (Muschelkalk) the SW part of Poland was situated in the SE part of the Germanic Epicontinental Sea. Full profile of Lower Muschelkalk was found in the SW part of Poland (area of Silesia- Opoliske Voivodesip). Formation contains strata of Gogolin Beds, Góra Ld Beds, Terebratula Beds and Karchowice Beds [1, 2]. The effects of destructive and constructive diagenesis were observed in Triassic limestone of Opoliske Voivodesip.

Discussion of Results

The effects of destructive diagenesis are longitudinal channels created by sea organisms and micritic coats in marginal areas of allochemes and peloides. Effects of eogenetic stage of constructive diagenesis are: first generation cement (micritic, orthosparitic and palisade), Mg- calcite, early diagenetic dolomite and clay minerals. During mesogenetic stage pseudosparitic, mosaic cement (second generation cement) was formed. It fills in the space in the rock between allochemes and builds together with the micritic cement the rock mass of limestone poor in allochemes. Neomorphic processes like transformation of aragonite into low magnesian calcite, recrystallization of calcite crystals which build the trochites of Crinoideas, recrystallization and agradation of crystals which build the cement and dissolution which caused the formation of stylolites fill in with the iron compounds, were also going during the mesogenetic stage. Telogenetic stage characterized by karst processes, dedolomitization and silification. Effects of karst processes are karst funnels and karst formations present in some areas of strata. During dedolomitization dolomite pseudomorphs were formed. During silification processes small pores in rocks were filled in with quartz or chalcedony and silica concretions, which create special levels in some limestone strata, were formed.

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Collection and measurements of reservoir fluids properties – ‘Today and tomorrow’

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Representative analyses of properties of hydrocarbon and non-hydrocarbon fluids in the petroleum industry strictly depend on the quality of the sub- or surface sampling. The exploration & appraisal activities in challenging pressure and temperature environments, as well as difficult fluids such as heavy oils, very high levels of H₂S or CO₂ require a completely new approach. Development and implementation of new technologies is a must, not a luxury.

Experience shows that the majority of non-representative data coming from laboratories are directly due to poor sampling practices and/or inadequate technologies employed. Recent improvements in sampling tools, include innovative approaches to prevent scavenging of H₂S, or absorption of mercury species, utilizing exotic materials such as Inconel 725, and inert coatings such as Dursan. The increased working range of sampling/analytical equipment is reaching pressures of 1700 bar (25 kpsi) and temperatures of 725°C to 170°C in water and CO₂, Gas-Oil Ratio, density, viscosity) in real time. The live developments of ‘downhole laboratories’ employing Grating spectroscopic tools such as LFA (Live Fluid Analyzer) led to breakthroughs in the mud gas logging are included an unprecedented leap from qualitative/comodity tools to quantitative fluid facies evaluation while drilling in C₁-6 range, including application of GC/MS and laser MS technologies for the methane stable isotope measurements.

The need for in situ measurements requires miniaturization and operational robustness. This article will discuss the latest advances in sampling and measurements along the fluid value chain – from the reservoir to laboratory.

Cadomian igneous rocks from Europe’s Variscan belt, Lazovo complex

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The geochemical and the age information contained in the Cadomian/Pan-African orogeny elements in Europe helps to identify portions of the Neoproterozoic-Cambrian plate boundaries [1]. In the Balkanides several types of such elements are known: some of the protoliths of Srednogorie high-grade metamorphic series - intermediate and acid igneous rocks ~590-620 Ma old [2]; Cherni Vrah ophiolite complex - ~560 Ma [3]; and 550 to 1100 Ma old inherited zircon cores detected in all high-grade metamorphic rocks.

We studied one of the easternmost exposures of the Variscan belt in the Balkanides in Tvarditsa mountain. The metamorphites of Lazovo complex cover wide areas of its southern slopes and host the pre-Triassic Tvarditsa pluton [4]. GPA geothermobarometry shows that amphibolite facies conditions were reached [5] in Variscan times [6]. The metamorphites in the eastern parts of Lazovo complex formed over intermediate to basic igneous protholites containing lense- and layer-shaped bodies of pyroxenites. They had different pre-Varsican metamorphic history compared to the garnet-bearing and the two- mica gneisses in the western parts of the complex [5]. The eastern part gneisses studied form thick layers of distinctive composition, not related to metamorphic differentiation. They preserve field and geochemical evidence of their magmatic origin. Their trace-element composition suggests subduction-oriented source.

The zircons from the gneisses studied and from the metapyroxenites have slightly elongated to rounded shapes. They display growth and sector zoning corresponding to igneous conditions of crystallisation. The U-Pb ages of the zircons obtained by LA-ICP-MS cluster at around 600 Ma.

Our data constrain for the first time the protholith age of Lazovo complex metamorphites and allow better correlation with the Neoproterozoic terrains in Eastern Europe.

Tracing magma chambers in the lab:
A case study on Lascar volcano

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Lascar volcano is a calc-alkaline stratovolcano located in the Central Volcanic Zone (CVZ), Northern Chile and represents the most active volcano in this area. The activity of Lascar is characterized by extensive lava flows, domes, and pyroclastic deposits such as the most recent eruption in 1993. Present activity is restricted by vigorous degassing from the open vents. The composition of erupted rocks of Lascar range from poorly porphyritic mafic andesites to dacites.

In this study we combine geochemical analyses with high P-T experiments to investigate possible depth of storage from the pre-eruptive conditions of crystallization on the one hand, as well as the role of magma-mixing and differentiation during magma ascent on the other.

Well-established geo-thermo- and barometers were used to characterize the crystallization conditions of the recent 1993 eruption. Results give evidence for a large temperature interval of crystallization from ~ 850 to 1050°C and pressures between 400 to 500 MPa. Oxygen fugacity was in the range of 1.0 to 2.0 log units above the Ni/NiO oxygen buffer. The analyses of melt inclusions are dacitic to rhyolitic in compositions with rather small concentrations of chlorine, fluorine and sulfur, indicating that the evolved magma was largely degassed.

The major element compositions of Lascar lavas indicate significant changes in the magmatic processes with the alternation of mixing- and fractionation-dominated stages. The compositional variation of deeper magmas (~ 1.3 ± 0.3 GPa) can be reconciled with magma mixing models. The compositional variations of most lavas erupted in 1993 and of a few older samples correspond to crystal fractionation trends, which have been reproduced experimentally at 300 to 500 MPa. Experimental data, geochemical trends and thermo-barometric data indicate that the pre-eruptive depth of the youngest magmas (< 7.1 ka) is rather shallow (~ 500 ± 200 MPa). A possible interpretation of these results is that magma storage in upper crustal levels is mostly dominated by fractional-crystallization whereas deeper magma chambers show clear evidence for magma-mixing processes.

Upscaling pore scale carbonate precipitation rates to the continuum scale

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An integrated approach combining experimental reactive flow columns and continuum-scale reactive transport modeling has been used to compare microscopic and bulk (upscaled) rates of carbonate mineral precipitation. The experiments consisted of the injection of supersaturated, carbonate-rich solutions into calcite packs. Bulk rates of precipitation based on the change in chemistry over the length of the column were compared with spatially resolved determinations of carbonate precipitation using X-ray synchrotron imaging at the micron scale. These data are supplemented by well-stirred reactor experiments to evaluate the rate of precipitation as a function of solution supersaturation in the absence of transport effects. Results indicate good agreement between rates determined with fluid chemistry and with microtomography. The distribution of calcite precipitates shows a nonlinear spatial profile, with the greatest accumulation near the column inlet. Precipitation is greatest on Iceland spar seeds, with crystal morphology of the new precipitates suggesting growth via a 2D heterogeneous nucleation mechanism.

Using the rates of precipitation as a function of supersaturation determined in the well-stirred flowthrough reactors, it is possible to match the spatially-resolved microtomographic data with a continuum reactive transport model if the generation of new reactive surface area is accounted for. The experimentally-determined value of 0.90 m²/g for the specific surface area of the neoformed calcite, added to the initial calcite surface area of 0.012 m²/g, results in good agreement with the continuum model. The approach used here also demonstrates that it is possible to determine upscaled reactive surface area in porous media if the intrinsic rate (per unit surface area mineral) is known.
Nickel isotope anomalies:
Neutron-rich or neutron-poor?

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The solar system is a mixture of many different nucleosynthetic sources. Numerous studies have investigated the nucleosynthetic origins of the solar system by examining isotopic anomalies in meteorites [e.g. 1]. Isotopic anomalies in the most neutron-rich isotopes of Ca, Ti, Cr in primitive meteorites have been interpreted as incomplete-mixing of a highly neutron enriched nucleosynthetic source into the early solar system [2-4]. This source has been variously hypothesised to be a type Ia supernova [5], type II supernova [6] or an AGB star [7]. However, nearly all of the reported anomalies have employed normalisation to a pair of lighter-isotopes, assumed not to be anomalous. Hence, in these cases the inference of a neutron-rich anomaly is a point of interpretation since the anomaly could equally well reside on one of the normalising isotopes.

More recently, Ni has been added to the list of elements exhibiting anomalous isotopes in its most neutron-rich isotopes, 60Ni and 64Ni [8, 9, 10]. We have made further measurements of these anomalies have employed independently (internally-normalised) and mass-dependently (double-spike), to yield absolute Ni isotope ratios that will better constrain the nucleosynthetic environment from which this incompletely mixed component arose. Preliminary results suggest that, in fact, the anomalies reside on 60Ni and not on 64Ni or 68Ni. If these findings of neutron-poor anomalies are confirmed, they have far-reaching implications for the nucleosynthetic sources of the Ni isotopic anomalies and the identification of the nucleosynthetic sources of the solar system in general.

Aqueous alkali silicate fluids can significantly contribute to the mobility of high field-strength elements in the lower crust and upper mantle [1]. The speciation of silica in these fluids is important for understanding the transport of such elements as alkali-silica complexes. Speciation of aqueous fluids and melts in the Na2O-SiO2-H2O system has been previously studied in situ for one composition on the H2O-NS4 join [2]; here, we investigate silica speciation of fluids over a range of compositions in the Na2O-SiO2-H2O system.

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The speciation of dissolved silica in aqueous sodium silicate solutions has been studied in situ up to 600°C and 2 GPa using Raman spectroscopy and a Bassett-type hydrothermal diamond-anvil cell [3]. Starting materials were either aqueous NaOH solution plus quartz, or water plus sodium silicate glass (NS2 and NS3), yielding bulk compositions from 10 to 70 wt% SiO2 and various Na/Si ratios. Composition was determined from the dimensions of the sample chamber and the quartz or glass chip, and the densities of the individual phases. The cell was heated until all phases except zircon were dissolved to yield a single fluid phase, which permitted analysis at known fluid composition. Pressure in the cell was determined from the shift in wavenumber of the v1-SiO2 (~1008 cm⁻¹) band of zircon [4].

The assignment of Raman bands to particular dissolved species remains somewhat elusive, so the interpretation is partly qualitative. The main trends observed in Raman spectra of fluids with increasing SiO2/H2O ratio include 1) decrease in the intensity of the ~770 cm⁻¹ band (monomer); 2) increase in the intensity of the ~1050 cm⁻¹ band (assigned to bridging oxygen Si-O stretch [2]); and 3) increase in spectral contributions at ~550-600 cm⁻¹ and ~830-1000 cm⁻¹, which have been assigned to Q² species [e.g. 2]. These trends are interpreted to represent increasing polymerization. Opposite trends, interpreted to indicate decreasing polymerization, are observed with increasing Na/Si ratio.


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Structure and function of microbial communities associated with low-temperature hydrothermal venting and formation of barite chimneys at Loki’s Castle vent field

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Structure and function of microbial communities associated with barite chimneys in a low-temperature diffuse venting area at the Loki’s Castle black smoker vent field at the Arctic Mid-Ocean Ridge (AMOR) were studied by 454-pyrosequencing of PCR amplified 16S rRNA gene sequences and total community cDNA (270 356 reads). White microbial mats present on the barite chimneys, and associated with sibolignid tubeworms directly on the seafloor, dominated by Sulfurimonas comprising 86–96% of the rRNA-tags. mRNA-tags indicated that vent fluids rich in H2S (and barium) discharged into the sulfate-rich seawater supported a chemolithoautotrophic lifestyle where reduced sulfur species were oxidized by oxygen or nitrate. CO2-fixation proceeded via the rTCA-cycle. Scanning electron microscopy revealed that large amounts of thread-like extracellular polymeric material in the microbial mats acted as nucleation points for barite biomineralization. Anaerobic methanotrophs (ANME) of the ANME-1 clade (26%), and the GOM-arc1 group (14.3%) were dominating in the white chimney barite whereas the black flow channel harbored the most diverse microbial community including taxa such as Planctomycetales, 13.5%; Thiotrichales, 10.5%; Thaumarchaeota (MG 1.1. a), 9.4%; Pseudomonadales 7.2%; and Methylcoccales, 3.5%. Hence, indicating methane (aerobic/anaerobic), sulfur and ammonia oxidation and heterotrophic metabolisms as dominating processes.

High pressure and high temperature effect on the structural stability of smectites doped with rare earth elements

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Smectites are phyllosilicates with high cation exchange capacity (CEC) in the interlayers. For these and other features, smectites have been used in various parts of the world as secondary barriers for possible leak of liquids that contain radioactive elements in definitive deposits of nuclear waste disposal. In such case, radioactive cation could be captured by smectite through cationic exchanges. However, very little is known about the stability of smectite under high pressures and high temperatures (HPHT). Preliminary studies developed by our group in dioctahedral calcium smectites showed that the smectite structure is stable, remaining dioctahedral after processing up to 7.7 GPa and at room temperature. This work intends to replace the calcium of the smectite for heavy rare earth elements (REE) using the CEC characteristic of the smectite. We have achieved a cation exchange in smectite using La3+ as REE so far. Results in SEM/EDS showed that there was not more evidence of calcium in the sample after CEC procedures; on the other hand, a large amount of lanthanum was present. Our next step is to submit La-rich smectite under extreme conditions of pressure and temperature in order to investigate the structure and chemical changes. To achieve high pressures, hydraulic presses with boards of anvils with toroidal profile and diamond anvil cell (DAC) is being used. SEM, X-ray diffraction and FTIR in situ analysis will be performed on all samples.
The stability and structure of Mg\(^{2+}\) bicarbonate and carbonate ion pairs – An experimental and theoretical study

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The chemistry of Mg\(^{2+}\) in aqueous CO\(_2\) solutions is of fundamental importance, both with respect to the reaction mechanism of magnesium carbonate precipitation and in relation to sequestration of CO\(_2\) by carbonate mineralization.

In order to get insight into the coordination and stability of Mg\(^{2+}\) bicarbonate and carbonate ion pairs, a combined experimental and theoretical study was conducted. Potentiometric titration and UV-Vis-IR spectrophotometric measurements on dilute solutions were conducted and the stability constants for the MgHCO\(_3\)\(^+\) and MgCO\(_3\) (aq) complexes derived in situ at 10-100°C. In addition, density functional calculations were conducted on the hydration environment around the Mg\(^{2+}\), HCO\(_3\)\(^-\) and CO\(_3\)\(^{2-}\) and on the respective complexes.

The aquated Mg\(^{2+}\) ion is octahedral coordinated. Upon substitution of HCO\(_3\)\(^-\) or CO\(_3\)\(^{2-}\) with first shell waters, the coordination changed to five fold with important implication for further reactions and magnesium carbonate mineralization. At neutral to alkaline pH values, the MgHCO\(_3\)\(^+\) and MgCO\(_3\) (aq) ion-pair contribute significantly to the CO\(_2\) speciation in magnesite saturated to supersaturated solutions. Moreover, with increasing temperature, their stabilities increase. However, under alkaline conditions and with increasing temperatures, the solutions become brucite saturated limiting the availability of Mg\(^{2+}\) in solution for carbonate mineralization and ion-pair formation.

Fluids on the loose – Capturing meaningful geochronology in sulfides

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For generations, economic geology students have been taught to tackle the world’s giant ore deposits. If you aren’t studying an economically important deposit at an operational mine, the value of your work may be perceived as less important. This approach to understanding the non-unique pandemic phenomenon of metal-carrying, sulfur-bearing, and sulfide-precipitating fluids in the crust has stymied our progress in ore geology. We cannot glean crucial and fundamental relationships by simply acquiring more and more data from massively chaotic environments fraught by full-time chemical and physical disequilibrium. If we want to understandhow fluids are transferred in the Earth’s crust, where fluids originate and why they migrate, and how these fluids relate to the observed and unseen rock record, we must turn our attention to locations where fluids have left their simple and indelible mark in the geologic history. This is readily accomplished through study of small metallic-mineral occurrences, and in particular by application of Re-Os geochronology and tracer studies. Dating of many small sulfide-bearing deposits gives us detailed histories of terrane-scale fluid migration events, be they external additions or metamorphic rearrangements of existing volatiles.

As geoscientists we have no truly robust means to correlate through space without the component of time. Without absolute dating, we have no frame of reference beyond immediately visible stacking or cross-cutting relationships. Re-Os studies of sulfides in the Earth’s crust have taught us that (1) the duration of large porphyry-style mineralization is an unimportant question as it is different for every deposit and every district and will not help us find ore, (2) the age of sulfide mineralization should not be shoe-horned to agree with associated U-Pb ages for obvious reasons, and (3) excluding true porphyry-style deposits, the mineralization process, in its entirety, commonly spans tens of millions of years.

If you want to understand the ore giants in the world, step back and be sure you understand the less complicated varieties first. Less is more. Good questions demand the right analytical approach. Though easy access to geochemical data tempts us to adopt the get-more-data approach, this will not lead to clarity of understanding.
North Atlantic influence on rainfall in the Dead Sea – Sahel watersheds: Implication for abrupt Holocene climate fluctuations

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Observations of 19th and 20th century precipitation in the Dead Sea watershed region display a multidecadal, anti-phase relationship to North Atlantic (NAtl) sea surface temperature (SST) variability, such that when the NAtl is relatively cold, Jerusalem experiences higher than normal precipitation and vice versa. This association is underlined by a negative correlation to precipitation in the sub-Saharan Sahel and a positive correlation to precipitation in western North America, areas that are also affected by multidecadal NAT SST variability. These observations are consistent with broad range of Holocene hydroclimatic fluctuations from the epochal, to the millennial and centennial time scales, as displayed by the Dead Sea and Sahelian lake levels and by direct and indirect proxy indicators of NAtl SSTs. On the epochal time scale, the gradual cooling of NAtl SSTs throughout the Holocene in response to precession-driven reduction of summer insolation is associated with previously well-studied wet-to-dry transition in the Sahel and with a general increase in Dead Sea lake levels from low stands after the Younger Dryas to higher stands in the mid- to late-Holocene. On the millennial and centennial time scales there is also evidence for an antiphase relationship between Holocene variations in the Dead Sea and Sahelian lake levels and with proxy indicators of NAtl SSTs. However, the records are punctuated by abrupt lake-level drops and extensive expansion of the desert belt at ~8.1, 3.3 and 1.4 ka cal BP, which appear to be in-phase and which occur during previously documented abrupt major cooling events in the Northern Hemisphere. The catastrophic aridity at 3.3 ka cal BP caused probably the collapse of the late Bronze cultures at the Levant, Mediterranean and Nileland. It sends an important message for the future of modern human culture.

Si isotope signatures in soils by UV femtosecond laser ablation

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Si isotope fractionation during weathering is now commonly mapped at the catchment scale. But we still lack an understanding of the processes that set isotope ratios. These take place at the mineral/pore water interface. We present the first Si isotope data of the principle Si pools in soils determined by a UV femtosecond laser ablation system coupled to a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS). This approach provides the opportunity to obtain precise and accurate data (1) on bulk sample materials as fused glass beads or pressed powder pellets, (2) at the mineral scale in thin sections and (3) for solutions after Si separation and evaporation. We investigated two immatured Cambisol profiles developed on paragneiss and sandstone in the Black Forest (Germany), respectively, after the last-glacial maximum. Bulk soils show a largely uniform signature in both soil profiles, which is close to those of primary feldspar and quartz with 30Si value of around -0.4‰. Clay formation is associated with limited Si mobility and hence preserves the original Si isotope signature of parental minerals. Organic-rich environments can promote intense weathering, which lead to high Si mobilization during clay formation together with significant negative isotope signatures down to -1.0‰ in topsoils. Biogenic minerals, i.e. phytoliths, exhibit negative Si isotope signature of about -0.4‰, which is in the range measured for different European tree species. Their impact in bulk soil signatures is negligible but is likely important for the dissolved Si pool. These results can now be used to reconstruct weathering and Si transport processes in soils to identify the source of dissolved Si in soil and river waters, which are commonly enriched in heavy Si isotopes.
Failure of density functional theory for ground state calculations on TiO₂

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Electronic structure computations based on density functional theory (DFT) is playing an increasingly important role in the study of material properties, including high pressure properties that are relevant for Earth’s interior. The success of DFT-based computations has been limited by the failure of standard implementations of DFT to properly describe the transition metal-bearing oxides and silicates that are of great importance in the Earth’s mantle, especially for Fe-bearing compounds.

There is less appreciation of DFT failures for lighter transition metal-bearing materials. For SiO₂ it is documented that with the local density approximation (LDA) stishovite is predicted stable over quartz which is corrected by the introduction of the generalized gradient approximation (GGA) [1]. However, experimental structural parameters and physical properties of quartz are better reproduced by LDA [1]. Similarly, and not well documented, for TiO₂ DFT in any approximation predicts rutile stable over anatase, in conflict with calorimetry [2].

We have revisited the relative stability of TiO₂ anatase and rutile, as well as other crystalline phases, with highly accurate all-electron methods and various approximations to exchange and correlation, and confirm that rutile is always found stable over anatase. Also, computing harmonic zero point motion energy for the two phases from linear response phonon computations does not stabilize anatase. However, a strong anharmonic character of rutile lattice vibration is revealed that warrants further studies.

High pressure phase relations are better reproduced within DFT, and a proper sequence of high pressure phase stability is reproduced [3]. Zero pressure bulk moduli are all below 240 GPa, suggesting that there are no superhard phases of TiO₂. Higher coordination of high pressure phase leads to stronger localization of the Ti 3d states.


Detection of airborne radionuclides released during the nuclear accident at Fukushima Daiichi over Europe

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5“Ring of 5 (Ro5)” is an informal group dedicated to the survey of artificial radioactivity in the atmosphere

Atmospheric release of radioactivity after the nuclear accident at Fukushima Daiichi started on the 12th of March 2011. Within approximately 10 days contaminated air masses reached Europe. The long range transport resulted in a dilution of the activity concentrations in the air by a factor on the order of 10000 times compared to concentrations reported from Japan. With levels of some tens of mBq m⁻³ at the most, there has been no health safety risk in Europe. The dispersion of the radioactive traces over Europe were followed through the analyses of filters of more than 140 high-volume samplers. Rapid exchange of data was granted through the participation of many laboratories in a network called “Ring of Five (Ro5)” which is an informal information club started in 1983 for this very purpose.

Switzerland was situated at the edge of a corridor with higher levels and saw comparatively low maximum total ¹³¹I activities of around 2 mBq m⁻³. At the end of March the activity ratios of gaseous ¹³¹I/particulate ¹³¹I recorded in Switzerland were around 4 to 6, while the activity ratio of particulate ¹³¹I/¹³⁷Cs was roughly 10. Samples taken with airplanes in the upper troposphere as well as samples from a high altitude station at Jungfraujoch (3500 m a.s.l.) allowed to assess the vertical mixing of the radioactive traces. Temporal evolution of isotopic ratios such as ¹³²Te/¹³⁷Cs or ¹³⁶Cs/¹³⁷Cs helped to estimate the duration of the major emissions as well as the composition of the source term.

In Switzerland atmospheric deposition of radioactivity was very low with only a few Bq m⁻² for ¹³¹I. This lead to spurious contamination of grass and leafy vegetables (up to a few Bq kg⁻¹ fresh weight). Again, at these levels there has been no food safety risk.
Interactions of phosphate and phosphonate with the calcite surface

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Crystal growth mechanisms of calcite have been studied in detail in the past [1, 2]. The ability of calcite to adsorb P as phosphate from raw, sea and artificial water [3, 4] has been investigated intensively to recover P as a valuable nutrient [5]. Moreover, a detailed understanding of the interaction between phosphonates and calcite is of great interest for large-scale application as scale inhibitor, dispersant or chelating agent [6]. To date, understanding atomic-level processes that govern the kinetics of calcite growth with respect to phosphate and phosphonate anions is still incomplete.

As part of the ReCaWa joint project (Reactivity of Calcite/Water Interfaces), we investigate the sorption and coprecipitation processes of phosphate and phosphonate on calcite surfaces from (super)saturated calcite solutions. Solutions were prepared from p. a. grade chemicals (CaCl$_2$, NaHCO$_3$) in double distilled water (18.2 MΩ·cm), with pH adjusted to 8.2 and I=0.1 mol/L. Phosphate (H$_3$PO$_4$, Na$_3$PO$_4$·6H$_2$O) or phosphonate (etidronic acid, HEDP) were added in concentrations from 3–1000 µmol/L and 10–25 µmol/L, respectively. For batch experiments differing amounts precipitated calcium carbonate or limestone powder with varying specific surface area (SSA) and crystal morphology were added to the solutions. Additional and upcoming coprecipitation experiments under strongly defined conditions are performed using a mixed flow reactor (MFR) to allow coprecipitation of homogeneous phosphate or phosphonate containing calcite onto the calcite seed powder.

Experimental results show that phosphate uptake is a function of SSA and formation of HEDP precipitates dependent on the calcite morphology, respectively. Forthcoming analytical work includes the identification of different fixation mechanisms and phosphorus-containing phases using XRD and XAFS spectroscopy at grazing incidence.


Geochemistry of lamprophyres in rare-metal districts related to granitoids

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Lamprophyres occur occasionally in mafic-silicic dyke suites of rare-metal (RM) granitoids in Paleozoic provinces of Western and Central Europe, Central Kazakhstan, the Altai, and in Mesozoic provinces of Transbaikalia, Yakutia, Chukotka and Alaska, which host RM (Sn, W, Nb, Ta, Mo, Be) mineralization. We evaluate 190 whole-rock chemical analyses of lamprophyres and variable sets of trace elements in order to uncover any genetic relationships between the melts derived from metasomatized upper mantle and enrichment in RM and alkalies. The lamprophyres correspond to minettes and kersantites with minor spessartites, and have MgO/MgO+FeOTOT ratios up to ~0.75 indicate no substantial modification by fractionation or crustal assimilation. The Zr-Hf and U-Th ratios are not decoupled, and the Nb-Ta ratios approach the primitive mantle values. However, absolute concentrations of these elements, which are also considered to be the least mobile in aqueous fluids, show large to extreme enrichments: Zr (27-1420 ppm) in calc-alkaline lamprophyres [1], 193 ppm in the upper continental crust [2], Hf (3.5-36 vs. 5.2 ppm [1], 5.3 ppm [2]), Th (4-75 vs. 9 ppm [1], 10.5 ppm [2]), Nb (2-150 vs. 13 ppm [1], 12 ppm [2]), Ta (0-16 vs. 0.9 ppm [1], 0.9 ppm [2]). These levels in lamprophyres of the RM districts exceed the average abundances of some elements in calc-alkaline lamprophyres or in the differentiated upper continental crust by one to two orders of magnitude. They are also systematically enriched in F (0.04-2.85 vs. 0.11 wt % [1]), Rb (43-1490 vs. 70 ppm [1]), Cs (2.4-122 vs. 3 ppm [1]), Li (14-447 vs. 44 ppm [1]), and Sn (1-417 vs. 2 ppm [1]) partly due to superimposed greisenization. However, the overall enrichment pattern of lamprophyres and mineralized granites suggests that the source of some components in RM districts can be traced to mantle-derived melts, as previously proposed for the Cornubian province [1].

Experimental study of monazite/melt partitioning

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Monazite (LREE, Th)PO₄ is a common accessory mineral and the major host of LREE, Th and U in the Earth's continental crust. Monazite is stable to high temperatures and pressures and is thus a key phase for trace element redistribution during partial melting of crustal rocks. We performed monazite-melt partitioning experiments in a piston-cylinder press over the temperature range 750 to 1200°C and pressures of 10-50 kbar. The starting composition was a synthetic granite mix with about 8 wt% H₂O that was doped with trace elements corresponding to 0.5-3 wt. % of monazite. Experiments at temperature >800°C and pressure <30 kbar produced melt with monazite. At lower temperatures quartz and plagioclase also formed. At higher pressures, kyanite, coesite, jadeite, apatite, zircon and epidote group mineral start to crystallize. Monazite was produced in all experiments and formed small grains (<5μm across). Laser ablation-ICP-MS analyses of monazite-melt mixes were performed and the monazite composition was calculated using regression analysis. The concentration of some elements was also obtained with Electron Microprobe analysis. These analyses were in good agreement with the monazite compositions obtained by the regression method.

The LREE and Th concentrations of melts coexisting with monazite strongly increase with increasing temperature. The melt composition has less influence on these concentrations. Monazite solubility decreases by 30-40 % with increasing pressure. REE, Th, U, Y and As strongly partition into monazite, whereas other trace elements (Li, Be, B, Sc, Ti, V, Mn, Sr, Zr, Nb, Ba, Hf, Ta, Pb) have monazite/melt partition coefficients lower than 10. Monazite has the highest preference for LREE from La to Nd, with a decrease in partition coefficients for Sm, MREE and HREE. Difference in partitioning of of LREE and HREE tend to decreases with increase of temperature and decrease with increase of pressure. Th partition coefficients are 30 % higher than those for LREE and are independent of pressure and temperature. Partition coefficients for U are much lower than for Th and LREE.

The new experimental data provide a basis for calculation of fractionation of LREE, Th and U during fractional crystallization and melting in the presence of monazite at crustal conditions and in subduction zones.

Aerosol, clouds, precipitation, radiation, and climate;
A global perspective

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The cloud systems of our planet fundamentally shape our climate in the way they affect the flow of radiation in and out of the planet and in the way they connect key processes together to form the hydrological cycle. Despite the many years of cloud observations from space, we have not gained much insight into these key roles. Information about cloud particle size from satellite radiometers, for example, has been derived now for more than two decades but we still have not convincingly determined if this information is in fact related to real cloud physical properties. Nevertheless correlation between this remote sensing particle size information and aerosol content now serves as a basis for parameterization of the so-called indirect effects in climate models, a key tuning knob of climate model sensitivity. Similarly we have also observed precipitation from space for many years but have not been able to tie these observations to actual cloud physical processes and thus precipitation observations alone offer little real insight into how precipitation is likely to be shaped by the broader environment in which it forms. In this talk, we demonstrate that new observations now available for Earth orbiting satellites, when combined together, are advancing our understanding of the processes that connect aerosol, cloud and precipitation together and in turn provide a unique view on how these processes alter the planet’s radiation balance. New insights on the effects of aerosol on cloud physical properties will be described as well as how these in turn affect both the water and energy balance of planetary cloud systems. The relevance of these new insights to the climate system and climate change will be emphasized.
Evidence for the formation of a fluorapatite surface layer on nano-sized hydroxyapatite after the exposure to an aqueous solution

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Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂; HAP) is the main constituent of bones and teeth [1]. Its ability to take up fluoride is applied in dental care [2] but also for drinking water purification [3]. Even though much research has been performed on fluoride uptake on HAP [e.g. 4], it is not fully understood how deeply fluoride incorporates into the HAP crystal.

It is believed that fluoride adsorbs to the HAP surface and exchanges for the hydroxide to form the less soluble fluorapatite (Ca₁₀(PO₄)₆F₂; FAP) [5]. The uptake capacity of fluoride on the HAP crystal is controlled by the exposure time and pH of the system [4]. A simultaneous formation of fluorite (CaF₂) cannot be ruled out when calcium and fluoride achieve saturation concentration [6]. However, a dissolution of CaF₂ in favour of FAP recrystalization is likely.

Batch studies were performed at 25 °C to investigate the uptake of fluoride as function of pH and initial fluoride concentration on synthetic HAP over an equilibration time of 28 days.

The reacted solids were investigated by Fourier Transform Infrared Spectroscopy (FTIR), which provided estimates on weight percentages on FAP formation on HAP after 28 days. Nano Secondary Ion Mass Spectroscopy (NanoSIMS) and Transmission Electron Microscopy (TEM) analysis gave additional information for a thin layer of FAP on HAP crystals.

To our knowledge it is the first time that the presence of a fluoridated surface layer on a nano-sized HAP crystal was qualitatively and quantitatively determined by micro- and spectroscopic analyses.


Ice formation on atmospheric mineral dust particles

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Mineral dust particles are known to be efficient catalysts for the formation of ice in clouds. In recent field studies by our group at the Jungfraujoch in the Swiss Alps a good correlation of the concentration of ice nuclei with the concentration of large particles during Saharan Dust events at this location was found [1]. Similar results are available from other groups as well e.g. [2].

However, the influence of size, shape, chemical composition, and the modifications of some of these parameters through anthropogenic emissions of pollutants to the atmosphere on the formation of ice is still mostly unknown and needs to be investigated further. This is complicated by the fact that ice in clouds may form via different pathways or mechanisms (immersion freezing, deposition freezing, contact freezing) and the parameters determining their efficiency in forming ice are different.

In our lab we investigate these different ice nucleation mechanisms with individual experiments for the different mechanisms using mineral dust aerosols. In this paper, our recent results on the ice nucleation properties of mineral dust particles for immersion freezing, and contact freezing are presented and compared.

The analysis of the immersion freezing data is done by calculations based on classical nucleation theory (CNT) assuming different assumptions regarding the properties of the mineral dust aerosols. From this analysis, the presence of so-called active sites can be deduced at which the nucleation process takes place preferably [3]. CNT also predicts that ice nucleation is a statistical process and therefore time dependent. To proof this, we conducted a special set of experiments where the residence time in the nucleation chamber is varied between 3 and 19 seconds. The results are again analysed and compared against CNT calculations as explained above and suggest, that immersion freezing is indeed time dependant where the frozen fraction increases with residence time.

Uranium(VI) complexation with lactate and citrate in dependence on temperature (7-65°C)

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After disposal in nuclear waste repositories the chemical and migration behavior of actinides depends on many factors. It is estimated that maximum temperatures in the near field of a repository could reach 300°C in dependence on the waste forms [1] and the host rock [2]. Thus, for the long-term safety assessment, knowledge of the interaction of actinides such as uranium with inorganic and organic ligands at elevated temperatures is required. The amount of organic matter in a repository can be separated in humic substances and in low molecular weight organic substances. A not negligible component of low molecular weight organic substances is the group of carboxylic acid. For example, citric acid is used in nuclear reprocessing [3] and acetic, lactic and formic acid were identified in rock extracts and pore water of Opalinus Clay [4]. Reliable experimental data on the complexation of U(VI) in solution at elevated temperatures are still needed.

Therefore, we studied the U(VI) complexation by lactic acid (pH 3) and citric acid (pH 0-10) in the temperature range from 7 to 65°C. Species distribution and complex formation constants were determined by means of UV-Vis and time-resolved laser-induced fluorescence spectroscopy. In the U(VI) lactate system, we identified the formation of 1:1- and 1:2-complexes. In the presence of citrate, we could characterize five U(VI) complexes in dependence on pH value. The complex formation between U(VI) and these both ligands was found to be endothermic and entropy-driven. The complex stability constants of the U(VI) complexes increase with increasing temperature. This could lead to an increased mobility of U(VI) at higher temperatures.


Early differentiation of terrestrial planets: The relative importance of big impactors and small impactors

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Planetary accretion arises through discrete events but is often treated as if those events were so frequent and large in number as to produce a continuum (a mass flux and characteristic time interval of accretion). Although there have also been published models that study the effects of discrete large impacts, insufficient attention has been paid thus far to the differences that arise for delivering material through a large number of small bodies and delivering the same mass (at the same epoch) as a small number of large bodies (e.g. Earth or Moon-sized giant impactors). The nature of the impacts is different in respect of the depth to which melting takes place, the extent to which equilibrium is established between core forming materials and mantle materials, and the pressure range of equilibration. As a result, two accretion scenarios that involve identical sequences (timing and size) of impact events can have different outcomes (different Hf/W inferred chronologies, different mantle siderophile inventories, different initial core T, etc) according as to the physical models one uses to describe the outcome of different sized impacts. Contrary to what some of the current literature implies, this is not merely the issue of the timing of the last giant impact since multiple giant impacts can be responsible for a large fraction of the mass delivery. It is also true that one cannot ignore the background ‘drizzle’ of smaller bodies (implied by the dynamic friction in the Nice models for example). I will describe semi-quantitatively the range of outcomes according as to the range of possible accretion histories for the terrestrial planets in general but with particular emphasis on Earth. This will also require an update of our current understanding of the mechanisms of core formation and the nature of melting curves and magma oceans in the deep mantle.
The strontium stable isotope composition of seawater during glacial intervals

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The strontium (⁸⁸Sr/⁸⁶Sr) stable isotope composition of seawater reflects input from continental weathering and hydrothermal exchange at mid-ocean ridges, and output in carbonate sediments. It has been suggested that increased weathering of shelf carbonates accompanying the low sea levels during the last glacial maximum (LGM) will have enhanced the flux of light Sr (from carbonates) to the oceans. However, temperature and species dependent fractionation of Sr stable isotopes during incorporation into marine carbonate has to be quantified in order to accurately reconstruct past seawater compositions.

This study presents high-precision (⁸⁸Sr data, obtained using double-spike TIMS technique. Present-day seawater yields a (⁸⁸Sr composition of 0.356±0.007 (2σ m) with no resolvable difference between Pacific, Atlantic and Indian Oceans. Globigerinoides sacculifer from sites in the South Atlantic, covering a temperature range of ~10 °C, show no systematic variation with temperature. Both G. sacculifer and G. menardii show systematic variations with growth rate (shell size) with heavier compositions in the larger size fractions. By contrast, G. aequilateralis and G. ruber show with no systematic variation with shell size. Preliminary (⁸⁸Sr data for G. ruber covering the last 70 kyr indicate that there was no resolvable change in the (⁸⁸Sr composition of seawater across the LGM and deglaciation. In this case the postulated enhanced weathering of shelf carbonates during glacial intervals [1], delivering light Sr isotopes to the ocean may not have been as significant as predicted [2] or else was offset by increased production and preservation of carbonates, driving seawater to heavier (⁸⁸Sr values. Alternatively the very long residence time of Sr in the oceans may simply buffer the changes in input or output such that no changes are resolved at the level of precision of this study.


Pb and Sr isotopes and the provenance of the painting materials in 19th century Canada

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Introduction
Cornelius Krieghoff was a 19th century Canadian artist (1815-1872) of winter landscapes and depictions of aboriginal and rural Quebec life. Like many pre-20th century artists, Krieghoff used a pigment known as lead white composed of a synthetic analogue of hydro-cerussite, often with lead carbonate impurities. Krieghoff used lead white in the preparation layer on the canvas and as a white pigment (either alone or in mixtures to lighten other colours). Calcium carbonate was often added as an extender. Samples of lead white and other Pb-bearing pigments of 15 Krieghoff works painted between 1844 and 1871 were also analysed for Pb and Sr isotopes to provide constraints on pigment sources.

Results
The bulk of the lead isotope data yield isotopic compositions that are consistent with data obtained from lead white in European paintings of the same or earlier periods [1, 2]. However, a few samples yielded lead isotope compositions that were more suggestive of a North American origin. The Sr isotope ratios of the samples range from values consistent with Palaeozoic carbonates to values in excess of present day seawater.


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Origin of dissolved metals in produced water from the Devonian Marcellus shale, USA: Sr isotope systematics

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The horizontal drilling and hydrofracturing techniques used for extraction of natural gas from shales of the Marcellus Formation (USA) lead to production of significant volumes of high-TDS (total dissolved solids) waters that have interacted with the source shale and potentially adjacent units. Determining the source of these dissolved salts and understanding local and basinal variations in TDS have direct relevance to exploration methodologies and water management and reclamation.

A series of flowback waters have been collected from drilling operations in a geographic region spanning ~375 km, from northeastern to southwestern Pennsylvania. Most 87Sr/86Sr values fall within a narrow range, from 0.7101 to 0.7112; samples from two adjacent wells in Westmoreland County, Pennsylvania, define a second grouping (0.7120-0.7121). This bimodal distribution of flowback values could be a result of hydrofracturing water interacting with different producing members of the Marcellus Formation, or lateral (facies) variations in the isotopic composition of formation salts. The relatively tight clustering of values among geographically distant sites argues against variable influxes of brines from adjacent formations. Marcellus flowback waters contain notably elevated levels of barium and strontium (up to 12,000 and 5,000 mg/L, respectively, for the samples in this study). The Ba/Sr ratios of the flowback fluids measured here also vary systematically with geographic location. The combination of Ba/Sr and 87Sr/86Sr provide a method for uniquely identifying regional variations in flowback waters.

The 87Sr/86Sr ratios of Marcellus waters measured here fall well above Phanerzoic seawater values. Thus, while the Marcellus brines may have a significant seawater component, this has clearly been augmented by a high-87Sr/86Sr source, possibly originating from dissolution of radiogenic minerals within the shale. Ongoing leaching studies of core material from the Marcellus Formation and adjacent units will provide additional insight into the origins of salts in Marcellus waters.

Evolution of andesite magma systems; Egmont Volcano, New Zealand

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A major issue in andesite magmas genesis is explaining disequilibrium crystal, matrix glass and whole rock compositions. Taranaki/Egmont is a high-K andesite volcano in the western North, Island, New Zealand, with a 200,000 year eruption record. Thirteen recently identified and dated pre-7 ka debris avalanche deposits record the magmatic evolution of the Taranaki volcanic system. Clast compositions show a gradual enrichment in K2O and LILE with time to high-K andesites in the Holocene. Pre-100 ka magmas include relatively primitive basalts and basaltic andesites and mineral chemistry indicates crystallisation within the lower crust or mantle. Modal rock compositions become more silicic in younger units, and the appearance of late-stage low-pressure mineral phases (high-Ti hornblende, biotite and Fe-rich orthopyroxene), suggests an increase in more evolved magmas with time. Six compositionally distinct Holocene magma batches erupted on 1500-2000 year timescales, synchronous with variations in eruptive frequency in which the largest volume (>0.5 km3) events erupt the most evolved magmas. We suggest that andesite magmas were generated within a lower crustal ‘hot zone’ [1]. Matrix glasses in both xenoliths and lavas/tephras are mostly dacitic to rhyolitic in composition and, in younger lavas have a high K2O content. These glasses may represent some of the partial melts from the ‘hot zone’ [2]. The disequilibrium observed in the andesites is due to the mixing of these diverse components. A complex and dispersed magma assembly and storage system developed in the upper crust where the magmas were further modified by fractional crystallisation and magma mixing and mingling [2].

Contrasting halogen geochemistry of barren and mineralized breccias of the Sudbury Igneous Complex, Ontario

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The potential for the halogen elements (Cl, Br, I) to be used as geochemical indicators for contact-style Ni-Cu-PGE mineralization along the lower contact of the Sudbury Igneous Complex (SIC) has been investigated. Two environments - one barren, and the other containing economic magmatic sulphide ore systems - were compared. The studied host rocks to these deposits are polymict igneous-textured breccias, formed by partial melting of the Archean country rocks.

No significant differences in bulk major and trace element geochemistry of rocks between the environments aside from the halogen elements were observed. Two major differences in halogen geochemistry were recognized:

First, mineralized breccias show marked enrichment in I. This is thought to have resulted from the leaching of I from brecciated sulphides by hydrothermal fluids released during contact metamorphism and partial melting of the country rocks, and is unique to those breccias that host sulfides. The anomalous I can be detected for distances of up to several 100 metres from mineralized samples. This observation is consistent with experimental studies which show that I is the most compatible halogen in sulfide liquids [1] leading to I enrichment in environments where sulfide liquids crystallize.

Second, analysis of the soluble fraction (from fluid inclusions) of the halogens reveal that two distinct fluid end-members were trapped in the matrix of the breccias during their crystallization (as mixtures in primary fluid inclusions): a high Cl/Br fluid phase of probable magmatic origin (exsolved from the SIC), and a low Cl/Br fluid phase derived from fluid released during dehydration of hydrous minerals in the country rocks. Mineralized breccias contain a much higher proportion of the non-magmatic fluid end-member. This would suggest that footwall partial melting was a critical component to deposit development, possibly promoting sulfide saturation in this local environment or the transportation of ore metals in high salinity fluids of non-magmatic origin (e.g. groundwater, metamorphic fluid).


Sources and input mechanisms of hafnium and neodymium in surface waters of the Atlantic sector of the Southern Ocean

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The first combined dissolved hafnium (Hf) and neodymium (Nd) isotope and concentration data from surface waters of the Atlantic sector of the Southern Ocean are presented here. The samples were collected along the Zero Meridian (ZM), in the Weddell Sea (WS) and in the Drake Passage (DP) during RV Polarstern expedition ANTXXIV/3 and ANTXIII/3 in the frame of the International Polar Year (IPY) and the GEOTRACES program. The distribution of Hf and Nd concentrations is overall similar. However, at the northernmost station located 200 km southwest of Cape Town a pronounced increase of the Nd concentration is observed, whereas the Hf concentration at the same time is at its minimum indicating lower amounts of Hf than of Nd released by weathering of the Archean cratonic rocks of South Africa.

From the southern part of the Subtropical Front (STF) to the Polar Front (PF) Hf and Nd show the lowest concentrations (<0.12 pmol/kg and 10 pmol/kg, respectively), most probably due to the low terrigenous flux in this area and scavenging of Hf and Nd by biogenic opal. In the vicinity of landmasses the Hf and Nd isotope composition is clearly labelled by terrigenous inputs. Near South Africa Nd isotope values as low as εNd = -18.9 indicate unradiogenic inputs supplied via the Agulhas Current. To the south the Nd isotope compositions are relatively radiogenic (εNd = -8 to -8.5) towards the STF, within the Antarctic Circumpolar Current, in the Weddell Gyre and the Drake Passage. Near the volcanic Antarctic Peninsula the isotopic data show significant increases to εNd = 6.1 and εNd = -4.0. implying an enhanced release of Nd and Hf. The Hf isotope compositions in the study area only show a small range between εHf = 6.1 and 2.8.

The new data show that Hf can be a sensitive tracer for prevailing physical weathering conditions, which is not the case for Nd. Neodymium isotopes show a factor of five larger range than Hf isotopes, which confirms Nd isotopes to be a sensitive tracer for the provenance of weathering inputs to surface waters of the Southern Ocean.
Rapid seawater circulation through animal burrows in mangrove forests — A significant source of saline groundwater to the tropical coastal ocean

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A common approach for quantifying rates of submarine groundwater discharge (SGD) to the coastal ocean is to use geochemical tracers such as 222Rn and short lived radium isotopes, which are naturally enriched in groundwater relative to seawater and have well understood chemistries within the marine environment. They occur in both fresh (continental) and saline (marine) groundwaters and thus the water source is often ambiguous. Here, we present a detailed investigation into the tidal circulation of seawater through animal burrows using 222Rn and isotopes of radium in the Coral Creek mangrove forest, Hinchinbrook Island, Queensland, Australia. The study was conducted at the end of the dry season in a creek with no freshwater inputs. Significant export of radionuclides and salt from the forest into the creek indicates continuous tidally driven circulation through the burrows. Results demonstrate that the forest sediment is efficiently flushed, with a water flux of about 30 L/m² day of forest floor, which is equivalent to flushing about 10% of the total burrow volume per tidal cycle. Importantly, annual average circulation flux through mangrove forest floors are of the same order as annual river discharge in the central GBR. However, unlike the river discharge, the tidal circulation should be relatively stable throughout the year. This work documents the importance of animal burrows in maintaining productive sediments in these systems, and illustrates the physical process that supports large exports of organic and inorganic matter from mangrove forests to the coastal zone. It also illustrates the importance of considering saline groundwater sources when interpreting SGD radionuclide tracers in the coastal ocean.

Observationally constrained estimates of carbonaceous aerosol transport and radiative effects

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Atmospheric aerosols play an important role in the global climate system. Carbonaceous aerosols stand out through their potential to warm (through absorption and semi-direct effects) and cool (through scattering and indirect effects) climate, depending on their microphysical properties and regional distribution. Current global aerosol models vary drastically in simulated abundance, transport and radiative properties of carbonaceous aerosols and show significant biases when compared to observations [1].

To advance our understanding of uncertainties in global models we utilise observational profile data obtained during the HIPPO aircraft campaigns [2] to constrain the remote transport in two microphysical aerosol climate models, ECHAM-HAM [3, 4] and HadGEM-UKCA [5]. In addition to mass concentrations, the SP2 instrument retrieves information about the mixing state of black carbon, providing constraints on the structural representation in microphysical models. In synergy with absorption optical depth retrievals from the AERONET sun-photometer network, such observations provide a unique constraint on transport and abundance of carbonaceous aerosols.

Comparison of the standard and observationally constrained setups will demonstrate the reduction of uncertainty in the simulated radiative effects. Nudged simulations using sector-specific emission inventories will allow quantifying sectoral contributions and the additivity of the individual contributions to the total carbonaceous radiative effects.

The ash that closed Europe’s airspace: Part II, the physical aspects of the Eyjafjallajökull ash

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On 14 April 2010, when meltwaters from the Eyjafjallajökull glacier mixed with hot magma, an explosive eruption sent unusually fine-grained ash into the jet stream. It quickly dispersed over Europe. Previous airplane encounters with ash had resulted in sand blasted windows and particles melted inside jet engines, causing them to fail. Therefore, air traffic was grounded for several days. Concerns also arose about health risks from fallout, because ash can transport toxic elements such as fluoride, aluminium and arsenic. For this study, we compared samples of the initial explosive ash with ash from the later, more typical eruption. Using nanotechniques, custom-designed for studying natural materials, we explored the physical and chemical nature of the ash to determine if fears about health and safety were justified and we developed a protocol that will serve for assessing risks during a future event [1].

We used atomic force spectroscopy (AFS) to map the adhesion properties on individual ash particles. With X-ray photoelectron spectroscopy (XPS), we determined the composition of nanometer scale salt coatings. By oscillating an atomic force microscopy cantilever, to which a single ash particle had been glued, we could measure the mass of adsorbed salts with picogram (pg; 10^-12 g) resolution. The particles of explosive ash that reached Europe in the jet stream were especially sharp and hard, therefore abrasive, over their entire size range, from submillimeter to tens of nanometers. Edges remained sharp, even after 2 weeks of abrasion in stirred water suspensions. From the composition of the particles, we could predict that they would soften and melt at temperatures typical of a jet engine (1500 to 2000 °C).

This paper is the second of a two part presentation, where the first part, by Sigurdur Gislason, focuses on the Eyjafjallajökull eruption, grain size distribution and soluble salt coatings.


Biogeochemical cycling of cadmium in the Tasman Sea: Constraints from cadmium isotopes

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The biogeochemical cycling of cadmium (Cd) is likely to be an important component of the ocean’s biological pump, yet the processes controlling its uptake are poorly understood. Stable isotopes of Cd offer the potential to provide new insights into the distribution and cycling of marine Cd, as sizeable 0.1%-level isotopic fractionation in seawater has been demonstrated due to biological uptake by marine phytoplankton [1, 2]. Furthermore, Cd isotopes may prove to be a reliable proxy for past and present nutrient utilization in the oceans. However, the limited results to date reveal the complex interplay of biological uptake, particle ‘scavenging’, and the mixing of different water masses. Additional datasets are, therefore, required to gain insight into the processes that govern the marine distribution of Cd.

Using multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) combined with double spiking techniques, we report the Cd isotopic composition and concentration of depth profile samples collected along a longitudinal transect in the Tasman Sea during the SS01/2010 (‘PINTS’) voyage — a GEOTRACES Process Study. The sampling transect extended southwards from the sub-tropical Pacific Ocean to the Southern Ocean, characterised by a strong longitudinal gradient with respect to the supply of trace metal-bearing dust, phytoplankton biomass, and oceanic temperature. The Cd isotopic and concentration water column signatures are interpreted in the context of other trace metals and macronutrients that potentially colimit marine phytoplankton growth, as well as oceanographic parameters, such as phytoplankton biomass. These data help elucidate the sources and biogeochemical cycling of Cd in the Tasman Sea, the validity of the Cd/Ca paleonutrient proxy, and the potential of Cd isotopes as a proxy of past nutrient utilization in the oceans.

Depth- and pressure dependent permeability in the upper continental crust — Data from the Urach 3 geothermal well

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The 4500 m deep research borehole 3 at Urach (South Germany) has been extensively used for hydraulic testing of the crystalline basement since the late seventies. The data permit a general interpretation of the hydraulic properties of the crystalline continental upper crust at different depth intervals. The gneissic basement contains an interconnected fluid-filled fracture system.

Low-pressure hydraulic tests show that the basement on a larger scale can be described as a homogeneous, isotropic aquifer and this characteristic hydraulic behavior persists at least several hundred meters away from the borehole. This demonstrated homogeneity of the aquifer (or fluid reservoir), together with the highly saline water in an interconnected system of copious fractures is characteristic of the continental upper crust in general. On a smaller scale, however, the fractures, crossing the uncased sections in the borehole, define the flow-behavior locally. So, at the beginning of a hydraulic test the pressure data show the influence of wellbore storage and skin, followed by a linear and a bilinear flow-period, and later on by a pseudo-radial flow-period. The transmissivity of the bulk rock can be derived from the data of the pseudo-radial flow-period.

The complete set of test data shows that in the crystalline basement permeability decreases with depth. There is also evidence for pressure dependent hydraulic phenomena, in particular permeability is found to vary with pressure.

Numerous high-pressure tests, some with well-head pressures of > 600 bar were carried in the Urach 3 borehole. The test data clearly show a P-dependence of permeability. During hydraulic tests with well-head pressures above 176 bar permeability of the crystalline basement increases dramatically, showing the elastic reaction of the rock due to pressure. At pressures below 176 bar the hydraulic data show no significant elastic reaction of the rock. A mathematical description of the pressure dependent increase of transmissivity has been derived from the data.

How do mineral substrates affect calcite nucleation and growth?

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Calcite was precipitated in flow-through experiments at 25 °C from supersaturated aqueous solutions in the presence of seeds of calcite and six different silicates: augite, basaltic glass, enstatite, labradorite, olivine, and peridotite. The aim of the experiments was to determine how calcite nucleation and growth depends on the identity and structure of the growth substrate. Calcite saturation was achieved mixing a CaCl₂-rich solution with a NaHCO₃-Na₂CO₃ buffer in a mixed-flow reactor containing 0.5-2 grams of mineral grains. This led to a calcite saturation index of 0.6 and pH 9.1 for the reactive solution inside the reactor.

Although chemical conditions, flow rate and temperature were identical for all experiments, the onset of calcite nucleation and the amount of calcite being precipitated depended on the identity of the substrate. With calcite as the growth substrate, new calcite crystals formed instantaneously. Calcite nucleated relatively rapidly on olivine, enstatite, and peridotite (mainly composed of Mg-olivine). Scanning Electron Microscope images showed silicate crystals to be almost completely covered with calcite coatings at the end of the experiments. Less calcite growth was found on labradorite and augite, and least on basaltic glass. In all cases, calcite precipitation occurs on the mineral substrate and not adjacent to them.

These findings indicate that calcite nucleation and its subsequent growth depends on the crystal structure of the silicate substrate. Orthorhombic silicate minerals (olivine and enstatite) are the easiest for trigonal calcite to nucleate on. Monoclinic augite and triclinic labradorite show intermediate behavior, whereas basaltic glass with its non-ordered crystal structure is the least favorable platform for calcite growth. The results have implications for CO₂ mineralization in ultramafic and basaltic rocks [1] indicating that trigonal carbonates easier precipitate on crystalline rather than glassy rocks, but even glass surfaces can serve as a substrate for calcite nucleation.

A new methodology for an improved description of radionuclide retardation in safety assessments

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Conceptual model

In safety assessments usually the K_d concept with temporally constant values is applied to describe the radionuclide retardation in the far field of a repository.

In this study, the existing transport program r3t [1] used for large model areas and very long time scales has been improved. Implementing the smart K_d concept based on surface complexation allows to consider the impact of varying geochemical conditions.

The new methodology describes the sorption of radionuclides as a function of selected, important environmental parameters E_i such as pH, pCO_2, ionic strength, concentration of the cations Ca^{2+} and Al^{3+} and presence of characteristic mineral phases. The Gorleben site as a potential repository site in Germany has been selected as an exemplary case of application for a proof-of-concept.

Most of the individual parameters E_i were not available in r3t so far. Thus the transport of the respective substances as well as equations describing pH and concentrations of ions as a function of accessible mineral phases had to be implemented. Then the reactive transport model rNt can call pre-calculated K_d values for selected sediments for each time-space point. They are stored in a multidimensional matrix depending on the real geochemical conditions. Figure 1 shows the frequency distribution of the pre-calculated smart K_d values for Am^{3+} and UO_2^{2+}.

Figure 1: Frequency distribution of the pre-calculated K_d values for Am^{3+} and UO_2^{2+} (in m^3/kg).


Combined NanoSIMS and TEM in situ analysis of pristine matrix material of ALHA 77307 and Acfer 094

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Only a few structural studies on presolar silicates and oxides exist [1]. Commonly the NanoSIMS mapping technique is used to identify presolar grains in the meteoritic matrix from a polished thin section. To extract these presolar grains for further TEM analysis, a complex and risky lift out procedure by FIB is needed [1], reducing the availability of such grains for structural studies. In contrast, Argon Ion Slicing (ArIS), a recently introduced TEM sample preparation technique in geosciences, yields super large electron transparent areas of up to 40,000 µm^2 [2]. The availability of extremely large thin foils makes a substantial change in the sequence of procedure steps possible, i.e. preparation of a large thin foil first, followed by the NanoSIMS scan on the previously obtained thin foil (Fig.1). No additional sample preparation for TEM is required once the grains are identified by NanoSIMS.

Figure 1: Thin foil section of ALHA 77307 with NanoSIMS scan windows indicated

Pieces of Acfer 094 and ALHA 77307 were ArIS treated until large electron transparent areas were obtained. These TEM thin foils were scanned for oxygen isotope ratios with a Cameca NanoSIMS 50. Based on large O-isotopic anomalies we detected 2 presolar grains (both silicates) out of 8 ion images (10 x 10 µm^2) in ALHA 77307, and 7 presolar grains (6 silicates and one oxide) out of 22 ion images (same size) from Acfer 094.

Multimethod characterisation of nanoparticles in the environment

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A range of techniques for the characterisation of nanoparticles will be presented, and their feasibility in studies of nanoparticle toxicity and environmental behaviour will be discussed. Techniques are often complimentary in the information they provide, and a multimethod approach is therefore recommended for nanoparticle characterisation. Results will be presented from the following studies, carried out at the Facility for Environmental Nanoparticle Analysis and Characterisation (FENAC) at the University of Birmingham:

1. Iron-rich and organic nanoparticles in anoxic groundwater, characterised under oxygen-free conditions by atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy with energy-dispersive X-ray diffraction (SEM-EDX) and field-flow fractionation (FFF).
2. Biogenic hydroxyapatite – relation between metal uptake and particle size/surface area, determined by X-ray diffraction (XRD), BET-surface area measurements, SEM, DLS and zeta-potential measurements.
3. ZnO nanoparticle dissolution and toxicity to marine invertebrates - dependency on particle size and morphology, characterised by TEM, AFM, dynamic light scattering (DLS), zeta-potential measurements and nano-tracking analysis (NTA).
4. Nanoparticle impact on bioremediation of hydrocarbons in aquatic ecosystems - relation to particle size and chemistry, determined by DLS, FFF, TEM and XRD.

Pore scale heterogeneity of porous media influencing the spatial and temporal distribution of microbial metabolic activity

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Microbial activity plays a crucial role in the cycling of carbon, nutrient elements and contaminants in the environment. This includes porous environments like soils or aquifers. These bacterial habitats are often characterized by a high temporal variability of substrate supply, and by a high spatial heterogeneity of the porous matrix at the pore scale. As a consequence, microbial growth conditions and the resulting microbial redox activity in natural porous media environments may differ from typical laboratory setups used to study microbial behaviour. Pore scale heterogeneities and the resulting transport regime can lead to highly complex distribution patterns of substrates and the corresponding microbial growth conditions including the frequent occurrence of stress periods for the microbial population. Microorganisms can respond to such stress periods by switching from an active into an inactive or dormant state, and the corresponding microbial abundance and substrate degradation dynamics may exhibit rather complex temporal and spatial patterns.

This study considers an extended modelling concept for the growth and degradation activity of microbial species able to switch between two different physiological states. This concept is implemented into a pore network model which allows simulating the changes of microbial growth conditions in heterogeneous porous media. The model is used to study the impact of pore scale heterogeneities on the distribution and activity of microorganisms in such media and to determine the biodegradation capacity of the microbial population.
Sources, sinks, and reactivity of electrophilic groups within natural organic matter

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Carbonyl and carboxylate ring substituents are believed to be present in high abundance within natural organic matter (NOM). Their potential impact on the reactivity of dihydroxybenzene/benzoquinone functionalities has not, however, been addressed. Owing to their electron-withdrawing nature, carbonyl and carboxylate ring substituents raise the redox potential necessary for oxidizing dihydroxybenzenes to corresponding benzoquinones. Carbonyl- and carboxylate-substituted benzoquinones generated in this way are far more electrophilic than unsubstituted analogs, and hence capable of Michael-type adduct formation with a wider range of oxygen-, nitrogen-, and sulfur-donor nucleophiles. Heightened electrophilicity also raises rates of competitive hydration reactions.

We have observed these phenomena in experiments employing low MW NOM surrogates. MnO₂ (pyrolusite) readily oxidizes acetoxyhydroquinone to acetoxy-p-benzoquinone and gentisate to carboxy-p-benzoquinone. Unlike unsubstituted p-benzoquinone, p-benzoquinones possessing electron-withdrawing groups rapidly hydrate. Adduct yields increase substantially as the nucleophile concentration is increased, a reflection of more successful competition relative to the hydration pathway.

Benzoquinones are one sub-class of conjugated ene carbonyls capable of Michael-type adduct formation. It is possible that oxidation reactions, e.g. by manganese(III, IV) oxyhydroxide crusts within oxic sediments, generate other reactive, transient electrophiles. Knowledge of their sources and sinks may improve our understanding of elemental and functional group incorporation into NOM.

Cosmogenic nuclide measurements of Pleistocene glacial erosion

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Glacial erosion plays a crucial role in landscape evolution at high altitudes and high latitudes, at the nexus between mountain building, surface processes and climate. Yet we lack a quantitative basis for incorporating glacial erosion into numerical models of these processes, and have few specific estimates of glacial erosion over 10⁵-10⁶ year timescales. We have developed a method of measuring past glacial erosion rates using cosmogenic nuclide depth profiles in bedrock. We are using this to determine glacial erosion histories, improve glacial erosion laws, and incorporate these into geomorphic process models.

Cosmogenic nuclide measurements on rock and soil surface samples have been widely used to estimate erosion rates in continuously exposed landscapes. Conversely, measurements on glaciated bedrock have been used primarily to date ice retreat, or, where such ages are compromised by prior exposure, to identify the sites as areas of limited glacial erosion. However, because the survival of nuclides produced beneath glaciated surfaces depends on subsequent glacial erosion, depth profiles accumulate information about the cumulative erosion history. Nuclide concentrations, concentration gradients and ratios are all sensitive to the history of exposure and erosion; we can use inverse methods to recover long-term average erosion rates of glaciated landforms from these data. Published cosmogenic nuclide measurements from glaciated bedrock surfaces suggest that these methods will be widely applicable to the study of mid- to late-Pleistocene erosion beneath glaciers and ice sheets.
Observational and modeling study of the relationship between aerosols and super-cooled cloud fraction

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Recent observational and modeling studies indicate that aerosols may have a strong effect on Earth’s energy budget via their influence on mixed-phase clouds. Global climate studies have predicted aerosol interaction with mixed-phase clouds to warm the current climate, but estimates are uncertain because mixed-phase cloud processes in GCMs are highly parameterized and have to date been poorly constrained by satellite data. Here, we present global and regional distributions of the frequency of supercooled cloud water and its link to aerosols from two global climate models (GCMs), compared to a new satellite data set. Both GCMs link ice formation at temperatures between -40 and 0 degrees C to the simulated concentrations of aerosols with ice nucleating ability (IN), assigning different freezing efficiencies to the different insoluble aerosol species (mineral dust, bio-aerosols and soot). Consequently, both models generally simulate an anti-correlation between aerosol abundance and supercooled liquid water in clouds, a finding that was recently qualitatively confirmed by satellite observations. By studying the relationship between aerosols and the supercooled cloud fraction (SCF) from the GCMs and from the NASA spaceborne lidar instrument CALIOP (cloud-aerosol lidar with orthogonal polarization), we get strong indications of how aerosols may influence mixed-phase clouds. We argue that with the new validation of SCF and its link to aerosols, GCM estimates of aerosol effects on climate via their influence on mixed-phase clouds may become more reliable.

The magmatic, metamorphic, mineralisation and plate tectonic evolution of continents

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Around 60% of continental crust was formed by the end of the Archaean and since then some form of plate tectonics has driven periods of supercontinent formation (at c.2.7 Ga, 1.9 Ga, 1.1 Ga and 0.35 Ga). Net growth of new crust declined in the Proterozoic and Phanerozoic and at the same time there has been a change in the mode of subduction from predominantly flat in the Archaean to progressively steeper towards the present day. This, along with the gradual cooling of the Earth, has resulted in marked changes in the preserved magmatic, metamorphic and mineralisation record. The first appearance of high-pressure metamorphic rocks, implying either overthickened crust or subduction, occurs in the Late Archaean around 2.7 Ga. There is a step-change in the magmatic products of subduction at the Archaean-Proterozoic transition from dominantly TTG through sanukitoid to calc-alkaline (basalt-andesite-diorite-rhyolite) as the main mode, which is most likely a result of a change in subduction angle and the development of a mantle wedge. This marks the onset of a form of modern plate tectonics. Whilst subduction magmas have been continuously produced they have also been continuously destroyed at continental margins, except at times when supercontinents formed, leading to pronounced peaks in crystallisation ages of detrital zircons. World-class ore deposits also correlate with the supercontinent cycle. During the Palaeoproterozoic (c.2.4-2.1 Ga) there was a period of anomalously low net continental growth followed by a peak of growth and mineralisation at c.1.9-1.8 Ga. We show how Fe-Oxide and related Cu and Au deposits can be linked to this cycle by measurement of Nd isotopes within titanite. The results imply that fertile mafic crust was incubated on the margins of the Archaean craton in the early Palaeoproterozoic but mineralisation did not occur until an arc was initiated at the margin and hence provided a heat and fluid source for mobilisation and concentration of the metals. The implication is that the formation and preservation of new continental crust is related to plate tectonics and the supercontinent cycle, which in turn controls the concentration and preservation of world-class ore deposits.
The mid-depth Δ¹⁴C anomaly during termination 1, Do hydrothermal vents play a role?

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The ~190‰ drop in surface ocean and atmosphere Δ¹⁴C during the last glacial termination cannot be explained entirely by Δ¹⁴C production change and thus appears to require a flux of Δ¹⁴C-depleted carbon into the upper ocean/atmosphere or a repartitioning of carbon in the ocean. A deglacial Δ¹⁴C stratigraphy from deep Pacific cores does not exhibit a -190‰ decline as observed in upper ocean records during the ‘Mystery Interval’ [1]. There are large benthic Δ¹⁴C-age excursions in several deglacial records from intermediate water depth cores at low latitudes but not in higher latitude cores [2]. These observations lead us to consider whether the flux of Δ¹⁴C-depleted carbon from hydrothermal sites in the Pacific played a role in the Mystery Interval Δ¹⁴C changes. Recent studies document liquid CO₂ and CO₂-rich fluids accumulation in sediments that blanket active vents. The storage and net flux of CO₂ from the sediments is regulated by the temperature dependence of CO₂-hydrate stability is a possible mechanism for affecting storage and release of CO₂ and CO₂-rich fluids from sediments. We explore a hypothesis where hydrothermal systems act as a ‘capacitor’ for CO₂ storage-release. CO₂-hydrate stability expands upward to shallower depths during glaciation, reducing the net flux of Δ¹⁴C-depleted CO₂ to the ocean. During deglaciation, CO₂-hydrate stability deepens, releasing Δ¹⁴C-depleted CO₂ from sediment reservoirs. A ~3°C temperature increase at intermediate depths in the Pacific during T1 would have lowered the hydrate stability horizon several hundred meters and released Δ¹⁴C-depleted carbon to the upper ocean/atmosphere. This would explain why abyssal water masses were not anomalously old during the last glacial and why the -190‰ decrease in Δ¹⁴C during the Mystery Interval is not observed at deep water sites.


Sampling the Earth’s mantle

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The Earth’s mantle is isotopically highly heterogeneous, certainly on the kilometer scale of the melting region, but perhaps even on a smaller scale. During partial mantle melting and melt extraction, instantaneous melts from a range of depths are mixed to different extents, eventually forming the melts sampled by oceanic volcanism. Mixing of partial melts from a range of different source components has an averaging effect that biases the isotopic composition of the melts compared to those of their mantle sources. The isotopic composition of oceanic basalts hence reflects only a limited extent of the isotopic heterogeneity present in the mantle.

The relative amount of melt mixing is reflected in the correlations between isotope ratios and different trace element parameters. For OIB, where melt extraction occurs over a short depth interval underneath a thick oceanic lithosphere, little melting of refractory, depleted mantle components occurs. Consequently, melts from the enriched mantle components do not become significantly diluted, resulting in few correlations between isotope and trace element ratios, but also a close correspondence of enriched melt and average enriched source signatures. In ridge-related settings, in the absence of a thick oceanic lithosphere, the depleted mantle components melt to a large extent, and the enriched melts are diluted significantly during partial melting and melt extraction. Melts from the enriched source components, however, still dominate the final erupted melt and obscure the true extent of mantle depletion in mid ocean ridge basalts (MORB). Hence the depleted components of the Earth’s mantle are expected to be isotopically more extreme than even the most depleted MORB.

Care must be taken, therefore, to extrapolate the isotopic variation observed in oceanic basalts directly to mantle heterogeneity. Before attributing the isotopic signatures of the basalts directly to those of the mantle, it needs to be understood how partial melting samples and averages heterogeneous source components. Only then can we infer the distribution of heterogeneous source components, their size, mineralogical, chemical and isotopic composition, which is a prerequisite for inferring the origin of the various heterogeneous materials in the Earth’s mantle.
Pb concentrations, stable isotopes and 210Pb in seawater, phytoplankton, zooplankton, sardines, anchovy from the Gulf of Lion

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Introduction

The COSTAS project aims at understanding the trophic transfer of metallic contaminants through seawater, phytoplankton, zooplankton, sardine and anchovy populations in the Gulf of Lion (NW Mediterranean). Its originality is to combine the ecology of the trophic web and the biogeochemistry of the metallic contaminants. We present here preliminary results of bioaccumulated lead in each compartment at four stations, which were emphasized by analysing for the first time and in the same samples 210Pb activity as a proxy of natural lead and 204, 206, 207, 208 Pb stable isotopes as proxy of anthropogenic Pb in the environment.

Results and discussion

Higher Pb concentrations in phytoplankton than in zooplankton (Fig 1) confirm the low ability of Pb to bioaccumulate in zooplankton. Pb isotopes ratios show different signatures among stations, despite constant Pb concentrations, close to the seawater signal in station far from the coast (St REF) and close to the radiogenic signal (1.175) in the Rhone station (St RHO). Emphasis on the relation between isotopes signals, Pb concentrations and plankton size/species will conduct to better understand the assimilation of Pb by plankton.

Review on biogeochemistry of microbial coal-bed methane

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Microbial methane accumulations have been discovered in multiple coal-bearing basins over the past two decades. Such discoveries were originally based on unique biogenic signatures in the stable isotopic composition of methane and carbon dioxide. Basins with microbial methane contain either low-maturity coals with predominantly microbial methane gas or uplifted coals containing older, thermogenic gas mixed with more recently produced microbial methane. Recent advances in genomics have allowed further evaluation of the source of microbial methane, through the use of high-throughput phylogenetic sequencing and fluorescent in situ hybridization, to describe the diversity and abundance of bacteria and methanogenic archaea in these subsurface formations. However, the anaerobic metabolism of the bacteria breaking down to methane substrates, the likely rate-limiting step in biogenic gas production, is not fully understood. Coal molecules are more recalcitrant to biodegradation with increasing thermal maturity, and progress has been made in identifying some of the enzymes involved in the anaerobic degradation of these recalcitrant organic molecules using metagenomic studies and culture enrichments. In recent years, researchers have attempted lab and subsurface stimulation of the naturally slow process of methanogenic degradation of coal [1].

Discussion includes description of (i) how occurrences of microbial methane accumulations in coal beds are identified through the use of geochemical tools such as stable isotopes; (ii) geological and hydrogeological constraints of such accumulations; (iii) the origin and composition of coal as the substrate and implications to microbial methane formation; (iv) methods of analysis of microbial metabolic pathways and microbial communities involved in biodegradation of various moieties of coal’s organic matter; (v) attempts of stimulation of enhanced microbial methane generation in coals.

Challenges to predicting the fate of emerging classes of organic micropollutants in subsurface environments

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Widespread detection of emerging micropollutants (e.g. antibiotics, hormones, personal care products) in soil and aquatic environments has raised serious concerns that necessitate improved understanding of processes controlling their environmental fate. However, existing models and reaction mechanisms are inadequate for predicting the fate of micropollutants that possess complex structures and functional groups not usually present in more commonly studied contaminants. Here, we describe recent efforts to characterize processes and mechanisms contributing to the fate of two widely detected classes of antibiotic micropollutants (sulfonamides, fluoroquinolones). First, we describe a novel microbially mediated-abiogenic transformation mechanism for the antibiotic sulfamethoxazole (SMX) in subsurface environments. Rapid dissipation of SMX is observed in iron-reducing soil microcosms, and mechanistic studies demonstrate that SMX transformation occurs via abiotic reactions of sorbed Fe(II) with an isoxazole group in the SMX structure, a moiety not previously reported to be amenable to reductive transformation in soil environments.

The complex poly-ionogenic structures of some micropollutants have complicated efforts to predict sorption and speciation in subsurface environments. For example, the unique characteristics of zwitterionic fluoroquinolone (FQ) structures (presence of both positively and negatively charged groups) lead to complex electrostatic interactions with charged surfaces that cannot be accounted for by isotherm or point-charge surface complexation models. Here, we describe the application of a charge-distribution (CD) surface complexation model for zwitterionic species sorbing to variously charged oxide minerals. Model formulation includes functional group-specific inner- and outer-sphere bonding interactions with mineral surfaces, in accordance ATR-FTIR spectroscopic observations. CD model predictions agree closely with measurements of FQ sorption to three oxide soil minerals (TiO2, α-FeOOH, and γ-AlOOH) collected over a wide range of pH, ionic strength and FQ concentrations.

Multiple sulfur isotopic evidence for multiple origins of late Archean and early Paleoproterozoic sediment-hosted pyrite, Quadrilátero Ferrífero of Minas Gerais

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Multiple sulfur isotopes were measured in different types of pyrite (detrital, frambooidal, euohedral, finely disseminated) from a late Archean to early Proterozoic metasedimentary succession in the Quadrilátero Ferrífero of Minas Gerais, southern São Francisco craton, Brazil. Samples derive from the Moeda Formation, a coarse clastic, metaglomeratic unit, and carbonaceous phyllite of the Batalat Formation. The Moeda Formation rests unconformably on Archean greenstone rocks and is conformably overlain by the Batalat Formation. The depositional age for both sedimentary units is bracketed between 2580 and 2420 Ma [1].

Multiple sulfur isotope results display distinct differences between the type of pyrite and the stratigraphic position of the host metasedimentary rocks. This offers the potential for resolving pyrite provenance and formation, for distinguishing prevailing metabolic pathways, and identifying the overall oxidation state of Earth’s atmosphere.

All pyrite samples show clear mass-independently fractionated sulfur isotopes, defining a slope of -1 in a $\Delta^{34}S/\Delta^{33}S$ plot. This confirms previously published data and underlines the interpretation of a low atmospheric oxygen abundance [2]. Combining $\delta^{34}S$ and $\Delta^{33}S$, detrital and euohedral pyrite from the Moeda metaglomerate exhibit largely positive values of $\Delta^{33}S$ (up to $+8\%$). In contrast, frambooidal pyrite from the Moeda Formation has negative multiple sulfur isotope values. Pyrite from the overlying Batalat Formation displays also mostly negative $\delta^{34}S$ and $\Delta^{33}S$ values. These results indicate at least two different metabolic pathways archived: microbial turnover of elemental sulfur and sulfate reduction.

Fluid-enhanced crystallization to generate high-S apatite of silicic magmas: Evidence from Pinatubo and other calc-alkaline systems

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We consider high-S apatites to be apatites with <0.7 wt.% SO3. High-S apatites of magmas with rhyolitic melt are of particular interest because experimental data suggest that such apatites are ‘over enriched’ in S relative to equilibrium crystall-melt partitioning processes. In Pinatubo dacite, 29% of all investigated apatites (N=69) include high-S concentrations. Conversely, the dominant apatite populations of silicic oxidized magmas are medium- (0.3-0.6 wt.% SO3) and low-S (<0.3 wt.% SO3) apatites (also at Pinatubo), which are consistent with crystallization from melt at or below S saturation at various temperatures.

Explanations for high-S apatites range from inheritance (from mafic magmas or country rock) to S exchange between apatite and anhydrite as a consequence of close petrographic association of both phases in systems containing anhydrite (e.g. at Pinatubo). The compositional fingerprint (e.g. REE, Sr) ties high-S apatites to the same melt environment as the dominant populations, and thus makes inheritance unlikely. Finding low-S apatite inclusions in anhydrite in conjunction with the lack of consistent rimward enrichment of S of anhydrite-hosted apatites, argues against S exchange between these two phases.

To generate high-S apatite, we envision a process that we call ‘fluid-enhanced crystallization,’ whereby the high-S signal is controlled by the presence of a S-rich fluid adjacent to a growing apatite while other compositional characteristics are mostly controlled by the silicic melt. This process would be consistent with observed reverse S zonation towards the rim, small scale and strong changes in S content within single grains, occurrence of low- to high-S apatites as inclusions together in single host minerals, and compositional similarity among low- to high-S apatites. At Pinatubo the existence of such S-rich fluid is corroborated by S isotopes of anhydrite as well as growth features of anhydrite. A suitable source for S-rich fluids would be fluids derived from degassing underplated mafic magmas.

Post-collisional magmatism during Variscan orogeny: The Furcatura pluton (Danubian domain, Romanian Southern Carpathians)

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Exploratory geochronological data indicate that the Furcatura pluton (312 ±2.8 Ma) was emplaced during the Hercynian orogeny. This late stage magmatism is essentially granitic/granodioritic, lacking associated basic rocks. Furcatura pluton (FP) is remarkably heterogeneous, showing wide ranges for most of the petrographical and geochemical parameters. The metaluminous to slightly peraluminous (average A/CNK of 1.04) granitoids are high-K (K2O/Na2O of 0.51-1.63) calc-alkaline, while some samples have shoshonitic affinity (maximum K2O of 5.61). They lack significant Eu anomalies (average Eu/Eu* of 0.94) and have subparallel REE patterns, with 2REE ranging from 51.11 to 203.7. The heterogeneous character of the FP is further reflected in the 18O values of the quartz separates, ranging from 7.37 to 11.59‰, with the highest values measured in the late magmatic aplitic veins. In conventional discrimination diagrams, as well as reflected by their trace elemental compositions, FP granitoids show both I- and S-type granite features. Geochemical evidence suggests the pluton was derived from a heterogeneous, primarily (lower?) crustal source, with subordinate additions of mantle-derived melts (e.g. low Nb/U and Ce/Pb). However, based on available data, contributions from a previously subduction-enriched mantle component can not be completely ruled out. Therefore, the FP granitoids may provide clues for deciphering the processes involved in the production of post-collisional magmas.
Study of candidate matrix-matched calibration standards for geological applications by nuclear and laser ablation based methods

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Laser ablation with induction coupled mass spectroscopy (LAICPMS) and laser induced breakdown spectroscopy (LIBS) became widely used in geological sciences. For quantification procedure of methods based on laser ablation, the matrix matched standards are required. Such standards, are largely lacking, especially for geological applications. We aimed at filling this gap by analyzing minerals, rocks, fused powdered rocks, sol-gel derived and plasmochemically deposited mineral analogues to identify possible candidate materials. The homogeneity and trace elements contents of the above mentioned materials were examined using µ-PIXE, LAICPMS-screening and by PIXE/PIGE/INAA techniques. Major/minor elements were studied using EPMA. PIGE is capable to detect some light elements that are not detectable by X-ray spectroscopic methods. INAA provides reliable informations about trace element composition of examined materials, with favourable detection limits compared with the majority of common analytical techniques.

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Constraints on Earth outgassing history from Ar isotope composition of Devonian atmosphere

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The noble gases have long been used to show that the terrestrial atmosphere resulted from the outgassing of the Earth’s interior rather than capture of the solar nebula during accretion. The primordial and radiogenic isotopes of the noble gases combine to make them a powerful tool for determining the time and tempo of Earth outgassing. Our understanding of the outgassing history of the Earth is largely derived from measurements of He, Ne, Ar and Xe isotope in samples of modern mantle, crust and atmosphere. Despite several attempts [1] there has been no unequivocal measurement of the isotopic composition of noble gases in ancient atmosphere.

We have now determined the Ar isotope composition of pristine samples of the 404 Ma Rhynie chert using a new multi-collector mass spectrometer and a low blank laser extraction technique. 40Ar/36Ar are systematically lower than the modern air value, and are not accompanied by non-atmospheric 38Ar/36Ar ratios. We conclude that the Rhynie chert has captured Devonian atmosphere-derived Ar. The data indicate that the 40Ar/36Ar of Devonian atmosphere was at least 3 % lower than the modern air value. Thus the Earth’s atmosphere has accumulated at least 5 ± 0.2 x 1016 moles of 40Ar in the last 400 million years, at an average rate of 1.24 ± 0.06 x 108 mol 40Ar/year. This overlaps the rate determined from ice cores for the last 800, 000 years [2] and implies that there has been no resolvable temporal change in outgassing rate since the mid-Palaeozoic. The new data require outgassing early in Earth history, and suggest that pristine samples of Archaean and Proterozoic chert may prove useful as palaeo-atmosphere tracer.

Glaciers: A window into anthropogenic perturbation of the global carbon cycle

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Glacier-derived dissolved organic matter (DOM) provides a significant source of ancient, yet highly bioavailable C to downstream ecosystems. The remnants of ancient peatlands and forests since overrun by glaciers have been invoked as a source of this ancient, labile DOM. Here we challenge this hypothesis, demonstrating that DOM exported from glaciers is predominantly anthropogenic and enters glaciers in a pre-aged form. C-containing aerosols, mainly from biomass and fossil fuel burning, are the original source of this aged-glacier DOM. Once deposited on glacier surfaces, aerosol DOM is exported downstream, providing an energy subsidy to aquatic ecosystems. As deposition of combustion products is a global phenomenon, we propose that all ecosystems are receiving this ancient, labile C subsidy. In vibrant ecosystems, the labile DOM windfall is presumably rapidly processed, its signal lost and impact masked. In frigid glacier environments, these inputs stand out, making glaciers sentinel ecosystems for the study of perturbation to global biogeochemical cycles through anthropogenic deposition. This deposition is predicted to increase in the future as emissions of combustion derived aerosols accelerates along with industrial growth.

Climatically driven changes in sediment supply on the SW Iberian shelf since the Last Glacial Maximum

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The assemblage of marine sediments on the SW Iberian shelf reflects various ambient particle sources that have undergone significant changes as a function of prevailing weathering and transport regimes since the Last Glacial Maximum (LGM). The relatively rapid, decadal scale Mediterranean overturning circulation permits mixing of suspended particles from the entire Mediterranean Sea. They are entrained into the suspended particulate matter (SPM) carried by Mediterranean Outflow Water (MOW), which enters the Eastern North Atlantic through the Strait of Gibraltar and spreads at intermediate water depth in the Gulf of Cadiz and along the Portuguese continental margin. Further major sediment sources that have potentially contributed to the budget of SPM along the flow path of MOW on the SW Iberian shelf are North African dust and river transported particles from the Iberian Peninsula. In order to reconstruct climate and circulation driven changes in the supply of sediments from these sources over the past ~23 000 years, radiogenic Nd, Sr, and Pb isotope records of the clay-size sediment fraction were produced from three gravity cores in the Gulf of Cadiz (577 m) and on the Portuguese shelf (1745 m, 1974 m). These records were supplemented by time series of clay mineral abundances and clay mineral ratios from the same set of samples. Contrary to expectations, the transition from the LGM to the Holocene was not marked by very strong changes of the source areas of the sediments deposited on the SW Iberian shelf. However, the Heinrich stadial 1 and the African Humid Period are marked by significantly different isotopic records. The data also suggest that the continental chemical weathering regime changed with prevailing climate conditions and supplied the SW Iberian shelf with variable clay mineral abundances from essentially the same source rocks.
High methane oxidation rates in ferruginous lake Matano

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Lake Matano is the 8th deepest lake on the planet and is the world’s largest known ferruginous basin [1]. This ancient lake is persistently stratified, and beyond its high Fe content, it is characterized by extremely low SO₄²⁻ and very high CH₄ concentrations. It has been proposed that CH₄ consumption in the lake occurs via a novel pathway in which CH₄ oxidation is coupled to the reduction of Fe and Mn (hydr)oxides [1]. To investigate the pathways of CH₄ consumption, we monitored methane oxidation rates with a ¹⁴C-CH₄ tracer, both with and without the addition of a suite of electron acceptors including Fe and Mn (hydr)oxides. Our initial measurements yield volume specific rates as high as 0.8 µmol l⁻¹ d⁻¹, comparable to modelled rates from C isotope and CH₄ concentration profiles [1]. Our measured rates, without added electron donor, are 7 orders of magnitude higher than those reported for the Cariaco Basin [2] and approximately 10 to 50 times higher than in Big Soda Lake, Nevada [3]. Considering the ultra-oligotrophic nature of Lake Matano, these are remarkably high rates. Electron acceptor addition experiments are in progress and these results will be discussed. Our results to date clearly show that CH₄ is an important component of the C cycle in Lake Matano and by extension ferruginous systems in general.


Laboratory experiments and modeling of CO₂ dissolution in water for carbon sequestration

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The injection of CO₂ gas in the dissolved phase is an alternative to that of supercritical CO₂ if the depth of the formation is <800m, or where immediate solution trapping is desired because of safety concerns. The most efficient way to dissolve CO₂ in water is downhole in order to take advantage of the increased hydrostatic pressure. We conducted experiments in a 100m long ‘well’ set up in the staircase of a Manhattan building to study the dynamics of the dissolution process. CO₂ was added at the top of the well with a sparger and the dissolution process was monitored downstream by image processing technology.

The experimental results reveal that bubble size and density decrease along the flow path as expected. However, the rate of dissolution decreased along the flow path with bubbles dissolving rapidly initially and extremely slowly afterwards. As the bubbles decrease in size, they became harder to dissolve, due to effects of rigidity of the gas-liquid interface and the presence of low solubility gases in the water and gas. The degree of dissolution could be considerably enhanced by using a passive mixer or an active downhole submersible pump. The dissolution process was simulated using the Darcy-Weisbach equation and a one-dimensional multi-gas numerical gas exchange model. Besides CO₂, common impurities such as N₂, O₂, noble gases, H₂, H₂S and gas tracers (SF₆ and SF₅CF₃) were included in the model. Extrapolation of the model parameters to real-world injection scenarios (e.g. the Carbfix pilot project in Iceland [1]) illuminate the role that the dissolved gas composition, the purity of the CO₂, and temperature play in controlling the efficiency of CO₂ dissolution for storage in geologic formations.

Geochemical and biological controls on the product of microbial U(VI) reduction

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Biores Remediation of the uranium-contaminated subsurface involves the reductive transformation of soluble U(VI) species to less mobile U(IV) species by the in situ stimulation of indigenous microorganisms. The U(IV) mineral uraninite, UO2(s), is considered the most desirable product of bioreduction due to its low solubility and high stability under reducing conditions. However, the formation of uraninite may be inhibited under certain geochemical conditions, leading to the formation of biomass-associated U(IV) complexes, referred to as monomeric U(IV).

In this study we examine the role of medium composition and extracellular polymeric substances (EPS) as inhibitors or promoters of uraninite precipitation. Uranium LIII edge X-ray absorption spectroscopy and a chemical extraction technique are used to differentiate between U(IV) species. It was previously reported that under controlled conditions in a simple medium containing bicarbonate and PIPES buffer at pH 6.8 (BP), the reduction of U(VI) by Shewanella oneidensis led to the formation of uraninite. In contrast, in a more complex Widdel Low Phosphate (WLP) medium, containing numerous salts, the reduction by the same bacterium led to the formation of monomeric U(IV). In the WLP medium, the presence of phosphate or calcium ions in the medium has a larger influence on the U(VI) bioreduction product, leading to an increase in monomeric U(IV) formation. Moreover, bacterial EPS production indirectly affects U(IV) speciation. The product of U(VI) reduction in BP medium by a mutant of Shewanella oneidensis deficient in EPS production was richer in monomeric U(IV) than that of the wild-type under the same conditions.

This work begins to explore the complexity of the factors influencing the product of U(VI) reduction. More in-depth investigation of the biological and geochemical factors influencing uranium bioreduction is warranted.
Quantitative identification of reservoir fluid properties and boundary shifts by laser-induced fluorescence

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In an oil-gas reservoir with multi-stage structural movement, both hydrocarbons and reservoir bitumen may have suffered from multi-stage mixture, alteration and deconstruction, which results in difficulties to reconstruct migration and adjustment histories of hydrocarbons due to many factors that affect the reconstruction. However, direct evidence for different phases of hydrocarbon migration, variations in oil-gas properties and shifts of oil-water boundaries could be obtained from fluid inclusions of oil-gas reservoirs, which can record primary components and temperature-pressure conditions of hydrocarbon migration and charge. Thus, the present study uses quantitative assessment parameters, such as fluorescence strength and maximum emission waves of organic fluid inclusions, to characterize parameters, such as fluorescence strength and maximum emission waves of organic fluid inclusions, to characterize parameters, such as fluorescence strength and maximum emission waves of organic fluid inclusions, to characterize variations related with oils, gases and water in reservoirs so as to reconstruct adjustment processes of hydrocarbon reservoirs.

The Tarim Basin in China has experienced multi-cycle structural activities, and several developed petroleum systems are vertically superimposed or horizontally distributed in the basin. The present research quantitatively investigates fluorescence characteristics of reservoir sandstones, delineates the difference in fluorescence characteristics for oil-bearing or condensate-bearing reservoirs using I_{max} (maximum radiofluorescence wave length) and \Delta \lambda (a wave length between 2/1 I_{max}), quantitatively analyzes the relationship between the primary oil-water boundary when hydrocarbon charge occurred and the present-day boundary, deduces reasons resulting in the elevation of oil-water boundaries based on structural evolution, and particularly, distinguishes dominant migrating pathways from all the oil-bearing reservoir beds according with the comparison of I_{max} (maximum radiofluorescence intensity) between present-day and old reservoirs. Therefore, the laser-induced fluorescence quantitative analysis can also play a significant role in investigating variations in paleo-oil-water boundaries, determining paleo-oil-column height, demonstrating oil saturation and wettability of reservoirs, and simulating displacement pressure of reservoirs as well.

Biodegradation of petroleum hydrocarbon in shallow groundwater from carbon and sulfur isotope evidence

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Biodegradation is one of main natural attenuation processes in petroleum hydrocarbons contaminated groundwater [1]. Carbon and sulfur isotopes may have been markedly kinetic-fractionated during biodegradation process [2], which provides a powerful tool to reveal mechanism of petroleum hydrocarbons biodegradation. In an oilfield area in Northeast China, oil-bearing saline water moves upward and infiltrates into the shallow groundwater resulting from the accident and the area of groundwater-contaminated plume is about 8000m². Concentration of Total Petroleum Hydrocarbons (TPHs), dissolved Inorganic Carbon (DIC) and dominant terminal electron accepters or donators, \(^{13}\)C\(_{\text{DIC}}\) and \(^{34}\)S\(_{\text{SO}_4^{2-}}\), have been analyzed.

Analytical results show that the spreading direction of contaminated plume is controlled by groundwater flow. And the concentrations of SO\(_4^{2-}\) and pH increase along groundwater flow in the central line of the plume while TPH and DIC decrease. The \(^{13}\)C\(_{\text{DIC}}\) values of the uncontaminated groundwater range between -9.5 and 8.0‰ PDB, while the contaminated is characterized by a significant depletion of \(^{13}\)C with \(^{13}\)C\(_{\text{DIC}}\) of -18.3~18.5‰ PDB. Furthermore, the concentration of DIC is negatively correlated with the value of \(^{13}\)C\(_{\text{DIC}}\). It is deduced that the increase of DIC results from the biodegradation of petroleum hydrocarbon in groundwater. Meanwhile, the \(^{34}\)S in the contaminated groundwater with the \(^{34}\)S\(_{\text{SO}_4^{2-}}\) of 25.0‰~48.1‰CDT is depleted to the uncontaminated groundwater with the \(^{34}\)S\(_{\text{SO}_4^{2-}}\) of 19.2‰~13.9‰CDT. The Rayleigh model calculation [3] shows that the biodegradation of petroleum hydrocarbon with the bacterial sulfate reduction has occurred in the contaminated aquifers.

The alteration sequence of PGM in the gossan of the Aguablanca Ni-Cu-(PGE) sulphide deposit, SW Iberia

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The gossan outcrops overlying the Aguablanca magmatic deposit [1] (situated in the Ossa-Morena Zone in SW Iberia) host significant total PGE contents of up to 5 ppm, with Pt and Pd dominant over Rh, Os, Ir and Ru. A detailed survey of the PGE distribution was carried out in this gossan in order to understand the processes that change primary magmatic PGM during weathering in an oxidising, low-T environment. PGE were investigated in host relic PGM (by SEM-EDS) and as traces in the host Fe-oxides and oxyhydroxides that form the gossan (by LA-ICP-MS) [2].

The study showed a gradual alteration of the PGM and release of PGE during the gossan formation, including: (i) initial breakdown of the already slightly altered, primary PGM [3] (24% of the total PGM located); (ii) formation of partially oxidised Pt-Pd-phases (3%), with a composition close to ‘PtO’ and ‘(Pt, Pd)O’; (iii) formation of numerous oxidised Pt- and Pd-(ε-Cu-Fe, Bi-Te)-phases (68%), with a composition usually close to ‘(Pt, Pd)O2’ and ‘(Pt, Pd)3O4’. Palladium-rich hydroxides were also identified. These phases all appear to have formed from alteration of earlier PGM to form pseudomorphs. Among them, Pt-rich PGM are more frequent and always appear better preserved than Pd-rich PGM; (iv) formation of Fe-Ni-Cu-(ε-Pt-Pd)-oxides (5%), mainly in patches that may include relic precursor PGM; and lastly, (v) incorporation of PGE into ferruginous supergene products, with a greater dispersion of Pd than for the other PGE. LA-ICP-MS analyses showed that Pt, Ir and Rh in oxides are mainly located close to sulphide relics. In contrast, Pd accompanied by Cu, Ni, Bi or Te, occur widely distributed within the different generations of Fe-oxides.

These observations suggest that the sequence of alteration of igneous PGM in a gossan is likely to be one of PGE-oxide formation followed by dispersion of the PGE into the Fe-oxides. This work adds to the understanding of the evolution of PGM in the surface environment.


Late-Cretaceous alkaline continental magmatism associated with Deccan Continental Flood Basalt sequences of Saurashtra in Western India

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The Saurashtra region in Western India consists of seven volcano-plutonic complexes (plugs) occurring within the Deccan Continental Flood Basalt of WDVP. The three major plugs occurring at Junagadh (Girnar), Bada and Alec Hills pipe-like igneous intrusions located along the E-W trending Narmada-Son lineament. Alkaline magmatism is represented by lamprophyres and nepheline syenites forming as minor composite intrusions which are spatially and temporally related and occur chiefly within the diorites in the upper part of the Girnar Complex. Nepheline syenite is generally cream coloured, spotted black and pinkish red with pyroxene and nepheline respectively and consists of a granitoid aggregate of alkali feldspar, nepheline, sodalite, cancrinite and aegerine. In lamprophyric sills, Cpx occurs as microphenocrysts of small rounded to prismatic crystals which show the characteristic oscillatory zoning (X_Mg = 0.65–0.77) and amphiboles which are of calcic variety (X_Mg = 0.48 to 0.65). X_an in plagioclase varies from 25 to 96. These alkaline rocks have higher concentration of total alkalies (8.0 to 14.57wt %), Al_2O_3 (22.2wt %), LILE and ΣREE as well as highly fractionated REE patterns. The available data suggest that they are products of fractionation of an alkali basic magma from which early crystallization of lamprophyres took place under high PH_2O conditions followed by nepheline syenites which crystallized at lower PH_2O under relatively dry conditions from the residual liquids. The occurrence of high MgO dykes (olivine tholeiites, Opx bearing pyroxenite dykes and ankaramite dyke), the essexite pluton and deep-seated lineaments coupled with the presence of strong positive gravity anomalies in the Saurashtra region reflect prevalence of an underlying sub-surface high density component in the Girnar and most of the other plugs in the region.

**Volume and ionic conductivity measurements of H$_2$O ice at high pressure and temperature**

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We examined isothermal volume (V) compression of H$_2$O ice based on in situ x-ray diffraction measurements at 33-79 GPa and 873 K, and its ionic conductivity at 20-60 GPa up to 920 K using impedance spectroscopy (IS) technique. High pressure (P) and temperature (T) conditions were generated by using an externally-heated diamond anvil cell. The anomalous volume reduction likely due to the hydrogen bond symmetrization was observed at 50-53 GPa and 873 K, while the previous study at room temperature reported that the highly compressible phase associated with the symmetrization is present at 40-60 GPa. There is no volume discontinuity in the isothermal compression, which contradicts the proposed first order P-T boundary between ice VII and superionic ice [2, 3]. In addition, in situ IS measurements shows that the ionic conductivity of ice monotonically increases with increasing T, and exhibits superionic conduction (>10$^{-1}$ S/cm) above 580-720 K at 20-60 GPa, which is the first experimental evidence of the superionic conduction in H$_2$O ice at high pressure. This suggests that superionic ice appears at sufficiently lower P-T than the proposed triple point.

Combining above results with the existing planetary isentropes [4], superionic H$_2$O ice is stable at P-T conditions corresponding to the interiors of Neptune and Uranus, the ice giants. The presence of superionic ice in these planets possibly accounts for the non-dipolar and non-axis symmetric structure of their magnetic fields.


**The system SiO$_2$-H$_2$O revisited:**

**Equation of state to very high temperatures and pressures including critical behavior**

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The system SiO$_2$-H$_2$O represents a simple model for metasomatism and hydrous melting in the lower crust and upper mantle. In this binary, the upper critical end point (UCEP), where complete miscibility between concentrated aqueous fluids and hydrous silicate melts occurs, is located at 1100 °C and 9.5 kbar [1], near the geothermal subduction gradient with important consequences for aqueous devolatilization vs. melt generation in the subducting slab. We have derived a new equation of state for aqueous silica, which combines intrinsic thermal properties of SiO$_2$ units with volumetric contributions resulting from solvent compression in the hydration sphere. The concentration scale is mole fraction, which enables the difference between standard states at infinite dilution and pure substance to be linked via excess energy of mixing represented by symmetric Margules term (W). In addition, the pressure-temperature locus of the UCEP provides two additional constraints on energy-composition relationships, thus reducing the effective number of independent parameters of the equation of state. The Gibbs energy of SiO$_2$ (aq) has the form: ΔG = a + bT + cTlnT + dP + eTlnP$_w$, where P$_w$ is the density of aqueous solvent at pressure and temperature of interest. The thermal part is assembled from constant enthalpy, entropy, and heat capacity, whereas the pressure term employs constant volume of the unhydrated species. Additional contribution arises from the pressure-volume work necessary to compress solvent molecules from bulk density to the density in hydration shell due to electrostriction, and it is related to solvent volumetric properties only [2]. The model was calibrated by 342 experimental quartz solubilities at 25-1100 °C and 0.001-20 kbar and ranging from 9 ppm to 70 wt.%, yielding a = -963.5 kJ mol$^{-1}$, b = 844.3 J K$^{-1}$ mol$^{-1}$, c = -124.1 J K$^{-1}$ mol$^{-1}$, d = 2.26 J bar$^{-1}$ mol$^{-1}$, e = -16.65 J K$^{-1}$ mol$^{-1}$, and W = 29.1 kJ mol$^{-1}$, with overall accuracy of 1.3 kJ mol$^{-1}$. In contrast to previous studies, our new model is capable of addressing SiO$_2$ behavior in dilute aqueous fluids and hydrous melts, including their supercritical mixtures.

Agriculture’s impact on the Si cycle by accelerated biomineralisation

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Biogenic silica plays a major role in the global cycling of silicon [e.g. 1] and in processes such as mineral weathering, soil acidification, and regulation of atmospheric CO2. Phytoliths form by silicon biomineralisation within plants (especially grasses) and constitute a major pool of biogenic silica. Biogenic silica production rates reported for natural vegetation communities have a mean of ~70 kgSiO2ha⁻¹yr⁻¹ [e.g. 2, 3, 4], but vary widely from only 2 kgSiO2ha⁻¹yr⁻¹ to up to 1,380 kgSiO2ha⁻¹yr⁻¹ for a tropical bamboo forest [5]. This data indicate a global silica phytolith production rate of ~1 billion tons of SiO2yr⁻¹ prior to agricultural development.

However, many agricultural crops and pastures are based on silica-accumulating grass species that produce silica phytoliths far in excess of that produced by most natural vegetation communities. For example, silica phytolith production rates in grass crops such as rice, wheat, sugar cane and bamboo are usually an order of magnitude greater than those observed for most natural vegetation communities [6, 7, 8] and can be over 3,000 kg per ha⁻¹yr⁻¹ [8].

Accelerated silicon biomineralisation consequent of agriculture not only results from higher silicon uptake within such crops but also by the increased biomass produced by agricultural practices such as fertilisation and irrigation.

Further factors that impact the global silicon cycle from this process include: 1) the large area being cultivated annually with high silica phytolith producing crops and pastures (e.g. ~0.7 billion ha under cereal crops alone), and 2) the slow turnover rates of silica phytoliths (e.g. >300 yrs under pastures) [e.g. 9, 10] and can be over 3,000 kg per ha⁻¹yr⁻¹ [8].

The recent discovery of pre-3.75 Ga metasedimentary rocks in the Nuvvuagittuq supracrustal belt (NSB) of northern Quebec, Canada, provides a new suite of rocks to further our understanding of Eoarchean Earth process. The NSB includes a CaO-poor (cummingtonite) amphibole, plagioclase, biotite, quartz and garnet-bearing mafic schist. The exact age and history of this rock is being debated: associated zircon ages give a minimum age of 3.77 Ga [1], and a ⁴⁰Ar/⁴⁰Ar isochron suggests that the NSB includes components as old as ca. 4.28 Ga [2].

Garnet Sm-Nd geochronology is a valuable tool to elucidate the tectonic and metamorphic histories of mafic rocks; recent improvements in sample preparation have improved both the accuracy and precision with which we are able to date the growth of garnet [3]. Although garnet dating in the cummingtonite amphibolite rocks will not resolve the age debate, it will tell us when the most recent garnet-forming metamorphic event occurred at which time Nd isotopes were last mobilized and exchanged among metamorphic phases.

After crushing and hand picking a visually clean garnet separate we performed partial dissolutions to remove micro-inclusions. Using a three step sequence of acids: concentrated HF, concentrated HClO₄, and 7N HNO₃, acid-cleansed garnets showed high ¹⁴⁷Sm/²⁴⁴Nd ratios (~6.0) indicating that low Sm/Nd micro-inclusions were eliminated. However, replicate preparations produced significant scatter in the isochron towards older apparent ages indicative of contamination from an older inherited high Sm/Nd inclusion phase (likely zircon). Adding a fourth aqua regia step to the partial dissolution sequence cleansed the garnet of these contaminants yielding slightly higher ¹⁴⁷Sm/²⁴⁴Nd (~6.1) and a robust three point garnet-matrix isochron age of 2574.70 ± 0.72 Ma (MSWD=0.77). This new age represents the youngest age associated with the NSB and implies the terrane underwent a final greenschist-amphibolite grade heating event after the final ca. 2.7 Ga crustal growth episode documented by metamorphic overgrowths on zircons [4].


2575 Ma age of Nuvvuagittuq metamorphic garnet

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The recent discovery of pre-3.75 Ga metasedimentary rocks in the Nuvvuagittuq supracrustal belt (NSB) of northern Quebec, Canada, provides a new suite of rocks to further our understanding of Eoarchean Earth process. The NSB includes a CaO-poor (cummingtonite) amphibole, plagioclase, biotite, quartz and garnet-bearing mafic schist. The exact age and history of this rock is being debated: associated zircon ages give a minimum age of 3.77 Ga [1], and a ⁴⁰Ar/⁴⁰Ar isochron suggests that the NSB includes components as old as ca. 4.28 Ga [2].

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Slab-derived halogens and noble gases with a marine pore-fluid signature

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Subduction volcanism is generally considered to form a 'subduction barrier' that efficiently recycles volatile components contained in subducted slabs back to the Earth's surface. Nevertheless, subduction of sediment and seawater-dominated pore fluids to the deep mantle has been proposed to account for the non-radiogenic elemental abundance and isotopic pattern of heavy noble gases (Ar, Kr, Xe) in the convecting mantle [1]. To verify whether and how subduction fluids preserve a seawater signature, we determined noble gas and halogen compositions of the exhumed mantle wedge peridotite and eclogite from the subduction-related Sanbagawa metamorphic belt, southwestern Japan, in which relicts of slab-derived water are contained as hydrous mineral inclusions or aqueous fluid inclusions.

The observed noble gas and halogen compositions of the peridotite [2] and eclogite from the subduction-related Sanbagawa metamorphic belt, southwestern Japan, in which relicts of slab-derived water are contained as hydrous mineral inclusions or aqueous fluid inclusions.

The observed noble gas and halogen compositions of the peridotite [2] and eclogite show striking similarities with marine pore fluids, challenging a popular concept that the water flux into the mantle wedge occurs only by hydrous minerals in altered oceanic crust and sediment. These results indicate that subduction and closed system retention of marine pore fluid occurs to depths of at least 100 km, necessitating a reassessment of the dominant transport mechanism and source of water in subduction zones. Further subduction of a small amount of marine pore fluid can account for the heavy noble gas composition observed in the convecting mantle.


Temperature controls of sulphur isotope fractionation during sulphate reduction by Thermodesulfobacterium and Desulfovibrio strains

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Sulphate reducers are known to fractionate sulphur isotopes during dissimilatory sulphate reduction. Unravelling the factors controlling the fractionation pattern would be essential to identify the contribution of each enzymatic pathway at the cellular level, interpret the isotopic signatures in geological materials, and track the sulphur cycling in natural occurrences. This study examined the sulphur isotope fractionation patterns catalyzed by a thermophilic Thermodesulfobacterium-related strain and a mesophilic Desulfovibrio gigas over wide temperature ranges.

The Thermodesulfobacterium-related strain grew between 34 and 85 °C with an optimal temperature at 72 °C and the highest cell-specific sulphate reduction rate at 68 °C. The isotope fractionation (\(\epsilon^{34}S_{\text{sulphate-sulphide}}\)) ranged between 9.1 and 25.7 ‰ over temperatures ranging from 51 to 77 °C. The fractionations remained at high levels for the growth above 55 °C and decreased significantly for the growth at 51 °C. The D. gigas grew between 10 and 45 °C with an optimal temperature at 36 °C and high cell-specific sulphate reduction rates between 30 and 36 °C. The isotope fractionation ranged between 8.5 and 52.0 ‰ over temperatures ranging from 19 to 39 °C and peaked at 24 °C. The relationships between the fractionation and temperature for two strains in this study in part resembled those previously reported for Archaeoglobus-related strains but distinct from those for D. desulfuricans, T. indicus and Desulfobacterium autotrophicum, suggesting that the isotope fractionation is controlled by the complex combinations of contribution from individual pathways. Measurements of multiple isotopes are warranted to reconcile the modelled uncertainty.
Soil water movement traced by oxygen isotope in the Mu Us sandy land, North China
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Soil water is very important to plant growth because of arid climate in the Mu Us sandy land. However, knowledge on soil water movement of this region is little till now. In this study, oxygen isotope compositions of soil water in the dune profiles at Henan Village are investigated and then soil water movement is explored.

Two dune profiles with the depth of 3.75m are bored at a about 12 h interval before and after a thunderstorm in the same site at Henan where average annual precipitation is about 400mm but average annual evaporation is up to 2000mm [1]. Soil water is extracted from samples after they are sent to the laboratory by the vacuum-distillation apparatus and then is analyzed for $^{18}$O via MAT253.

$^{18}$O value of soil water changes greatly between -0.96 and -7 in the upper part with the depth of about 1.8m but fluctuates constantly within a narrow range of -6 ~ -8 in the lower part of the first profile (before thunderstorm). $^{18}$O value of soil water also has a large variation from -2.87 to -7.54 in the upper part and a similarly narrow range in the lower of the second profile (after thunderstorm). The isotopic data have three implications: (1) the evaporation only impact water isotope in the upper profile with the 1.8m depth; (2) the thunderstorm event carries more negative oxygen isotopic composition into the upper profile; (3) since soil water in the lower profiles has $^{18}$O value more positive than that of local groundwater [2], they seem not to be of same origin. In addition, the average infiltration rate of this precipitation is about 15cm per hour through calculation.

As a result, the precipitation infiltration is only limited to the 1.8m depth under the land surface although there is a large amount of the precipitation for the thunderstorm event in a short time. It is thus inferred that vertical infiltration of the precipitation through the dunes might have little recharge to groundwater.


Geochronology of continental volcanic-type gold mineralization in East Tianshan, Western China: Constraints from Ar-Ar isotope of Shiyintan gold deposit
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The East Tianshan area in northwest China locates on the boundary between Tarim plate and Kazakhstan-Junggar plate. Both plates had experienced a complicated breakup and collision since late Precambrian, accompanied by large-scale thrust and continental volcanism [1]. Previous studies suggested two stages of continental volcanism: the first stage occurred between Late Carboniferous and Early Permian with isotopic age of 310~290Ma; the second stage occurred between Late Permian and Early Triassic with isotopic age of 260~240Ma. The Shiyintan gold deposit locates in the extensional tectonic-magmatic belt of Queleage in East Tianshan area, composing mainly of NO. W, NO. 9, NO. X ore bodies, with ores held by both gold-bearing quartz veins and altered andesite. Andesite, hornblende andesitic dacite, amygdaloidal andesite, volcanic breccia agglomerate lava and volcanic breccia of Permian are the exposed strata within mined area.

In order to study the metallogenic epoch of Shiyintan gold deposit, altered andesite ores were sampled from NO.I ore body, from which sericite is extracted for $^{40}$Ar-$^{39}$Ar isotope dating analysis by step-heating, yielding a plateau age (Tp) of 304.2±1.3Ma and isochron age (Tt) of 304.7±4.9Ma (initial ratio of $^{40}$Ar/$^{36}$Ar=292±10). This mineralization age of 304Ma in Shiyintan gold deposit is in great concordance with the age of ore-bearing volcanic rocks, deposition of gold occurred in extensional tectonic stage of post-orogenic between late Carboniferous Kazakhstan-Junggar and Tarim plates, developing in the extensional area of shear flank.

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Geochemical characteristics of the Shaxi-Changpushan porphyry Cu-Au deposit: Significance to ore formation

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Introduction
The Shaxi-Changpushan porphyry copper (gold) deposit is located in the northwestern Luzong volcanic basin. It also belongs to the north of the middle and low part of the Yangtze iron and copper metallogenic zone with the multiple location of faults, where Fanshan-Tongling deep fault and Tan-Lu fault belt come through the whole mineralization region and result in serious rock deformation in Jurassic [1].

Methods and Results
Based on geochemical studies and literatures [2-10], including chemical analysis on bulk rocks, rare earth and trace element studies, fluid inclusion, S and O isotopic analysis, we present significant proofs for the copper-(gold) mineralization in Shaxi porphyry copper-gold deposit. The sulfur isotope data show that the magma has the characteristics of deep source. Compared with the other large and supper-large porphyry copper deposits in China and the adjacent copper mineralized areas, ore-forming processes and conditions were analyzed. Our study indicates that the ore-forming fluids and materials were dominated with the magmatic origin, whereas the meteoric water played small role in the ore-forming processes. There are great potentialities to form a large porphyry copper deposit from the point view of tectonic evolution and geochemical characteristics in Shaxi-Changpushan Cu-Au ore district.

Oceanic Anoxic Events and Cenozoic large scale molybdenum mineralization

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Half of the world’s Mo reserve is hosted in Cenozoic porphyry-copper (Cu)-molybdenum (Mo) and porphyry-Mo deposits along the west coast of the American continents with nearly no Mo porphyry deposits along the west coast of the Pacific Ocean. In contrast, most Mo deposits in Eastern Asia are located along the Qinling-Dabie orogenic belt and in Northeastern China. Here we show that the large scale Mo mineralization along the west coast of the American continents is mainly due to the partial melting of Mo enriched sediments formed during oceanic anoxic events (OAEs) in the Jurassic and the Cretaceous. Porphyry-Cu-Mo deposits in the American continents are formed through partial melting of Mo-rich OAE sediments carried by flatly subducted oceanic crust in the east Pacific. High-fluorine (F) porphyry-Mo deposits are mostly located in the Colorado mineral belt (COMB), which are formed through direct partial melting of high grade metamorphosed Mo-rich OAE sediments in backarc settings, induced by the roll back of the flatly subducted east Pacific slab. Most low-F porphyry-Mo deposits have closer spatial relationship with porphyry-Cu-Mo deposits and are formed through partial melting of metamorphosed OAE sediments induced by arc magmas. In contrast, Mo porphyry deposits in Eastern Asia belong to low-F type, likely formed through partial melting of metamorphosed Mo rich sediments. Molybdenum deposits in Northeastern China were likely also due to Mo rich sediments formed during OAEs, whereas those from the Qinling orogenic belt were likely related to sediments formed in Triassic backarc settings.
Extraction time for soil water of desert sand used in stable isotope analysis

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Vacuum distillation has been widely used to extract soil water for stable isotopic analysis in studies of water cycle Distillation time is very crucial to complete soil water extraction. In this study, experiments of extracting water from dune sand of the Chinese desert are carried out to determine optimal extraction time.

Seven 30g sand samples with 10% moisture and known water isotopes are prepared and the distillation temperature is set at 105°C for the experiments of soil water extraction. The samples are vacuum-distilled for 4min, 8min, 12min, 16min, 20min, 25min and 30min, respectively (Fig. 1). Extracted water is analyzed for $\delta^{2}$H and $\delta^{18}$O by MAT253.

Figure 1: Isotopic variation of water extracted from sand samples.

As shown Fig.1, $\delta^{2}$H, $\delta^{18}$O decrease gradually with time. They arrive to zero (%) at 20min and then tend to be constant. This result indicates it need take at least 20min to completely extract soil water from desert sands. For different types of soils, the extraction time is distinct [1]. To be on the safe side, we suggest 28min for extracting water from sands in the Chinese deserts. Certainly, water extraction of over 30min is insignificant. Our conclusion agree well with West et al. (2006) [2].

Episodic events of the Western North China Craton and North Qinling Orogenic Belt, in central China: Revealing by detrital zircon U–Pb ages

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Detrital zircon U–Pb geochronology serves as a proxy to study of crustal evolution and provenance discrimination. In order to unravel episodic events and their tectonic relationship of the North China Craton (NCC) and North Qinling Orogenic Belt (NQOB), detrital zircons from modern river sands and metasedimentary rocks are collected and dated by LA-ICPMS. Although the western NCC (Ordos terrane) is covered by Mesozoic-Cenozoic basin sediments, the U–Pb dating results have shown that the age populations of detrital zircons from the western NCC with prominent U–Pb age peaks at 2475 Ma and 1850 Ma, which indicates the western NCC (Ordos terrane) also has early Precambrian basement similar to the eastern and central craton. In addition, a significant number of early Paleozoic (520- 400 Ma) zircons have been found in the western NCC, which is different from the eastern NCC and is considered to be related to the collision between the NQOB and the NCC.

The age spectra of detrital zircons from the NQOB presents a complex age pattern, which reveals four major age groups of Neoarchean (2.6–2.4 Ga), Neoproterozoic (1.0–0.85 Ga), early-middle Paleozoic (450-350 Ma) and early Mesozoic (250–170 Ma). As indicated by the U-Pb isotopic data that the NQOB could be an independent terrane at least prior to the Neoproterozoic and once a portion of the Grenville orogenic belt during the 1.2-0.8 Ga with a peak of ~1.0 Ga. In other words, the NQOB has its unique geological evolution history obviously different from those of the NCC and the Yangtze Craton. The complete collision between the NQOB and the NCC perhaps took place at Paleozoic (450-400 Ma).

Predicting reservoir fluid properties using absolute concentrations of canned cutting gas components

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The canned cutting gas data are the most frequently used geochronal approach to characterize reservoir fluid properties during petroleum exploration. Traditionally, canned cutting gas analyses are semi-quantitative and usually reported as C_1 through C_5 normalized, therefore increasing the uncertainty in respect to fluid prediction. Here, we developed a quantitative method for canned cutting gas analyses, and together with their carbon isotopic compositions and molecular parameters to identify reservoir fluid types and barriers.

The canned cuttings are received from the well site. Samples are routinely analyzed at intervals varying from 10 to 30m. A known volume of cuttings are homogenized with water in a gas-tight blender and a sample of head space is analyzed for methane, ethane, propane, butane and pentane. For absolute concentrations of cutting gas components, an internal standard is chosen and the relationship of GC response factor between standard and aimed gas components is constructed. By adding known amount standard into canned cutting system before GC analysis, absolute concentrations of canned cutting gas components can be calculated and reported as mol.

If neglecting the loss of gas during drilling and transport to surface, degassing efficiency is the most important factor to influence absolute concentrate of gas components, which strictly depends on temperature and its holding time and rock characters. Here, temperature and its holding time are investigated and the results show that concentration of gas components goes up with an increase of temperature up to 60°C and then keep stable, while the holding time is a not a significant factor where there is almost no change from 30min to 60min. Stable carbon isotopic compositions of gas components are less affected by degassing efficiency and this is in agreement with the observation by GeoMark.

A case study from the Panyu low-uplift of Baiyun depression, South China Sea is presented. Quantitative data, integrated with DST results, preliminary criteria can be made to define whether the oil and/or gas reservoir identified by normal logging is a commercial pay zone, and therefore for further DST planning.

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Experimental study of solution-mineral interaction in the Qisanba uranium deposit, NW-China

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Introduction

The Qisanban U deposit is hosted by a sandstone aquifer with groundwater whose TDS ranging roughly from 8-12 g/L. All the past pilot acid and alkaline in situ leach uranium mining tests failed due to serious chemical plugging during the mining processes. To develop a new solution mining technique, leaching test of uranium ores in ammonium bicarbonate solution was carried out. The TDS of the solution was maintained around 2 g/L by dilution using fresh water, and the pH was kept as 6.0-6.3 by pumping CO_2 into the solution.

Result and discussion

The experiments showed that uranium can be leached effectively from the ores in ammonium bicarbonate solution without any chemical plugging. A new bicarbonate solution uranium mining technique based on groundwater dilution may be proposed.

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First finds of ‘Alloclasite’ (Fe,Co,Ni) AsS in Ni sulphides of Bangur Gabbro, Orissa, India
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The diarsenides and sulfarsenides of Fe, Co and Ni have a widespread geological occurrence; they exhibit complex paragenetic and compositional relations, and are commonly associated with economically important minerals, such as PGM and gold. We found mineral phase consist of enriched amounts of (Fe, Co, Ni) (As, S)2 phases in Ni-S phases of Bangur gabbro in Orissa. The age of Bangur Gabbro is ~3.1 Ga. The eastern part of the Indian Shield is composed of a high-grade metamorphic terrain known as the Chhotanagpur Craton in the north and a granite-greenstone terrain known as the Singhbhum Craton in the south. The latter is mainly composed of several granitoid batholiths, which are largely surrounded and intervened by supracrustal rocks. Both Bangur and Baula (21°15’38” to 21°16’55” North and 86°.19’14” to 86°20’10” East) in the eastern part of Indian shield have been studied earlier by earlier workers [1], but petrological data (i.e. magma evolution and ore forming processes) are scanty. We report here the presence of mineral phase consists of (Fe, Co, Ni) (As, S), There is complete solid solution series exist between alloclasite- cobaltite- gresdorffite. The observed assemblages and solid solution agree well with experimental data on Fe-Co-Ni-As-S system.


Aerosol optical properties and direct radiative effect over India based on satellite remote sensing measurements
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Aerosols affect Earth’s radiation budget directly by scattering and absorbing solar radiation, and indirectly by modifying the microphysical properties of clouds. However, large uncertainties still exist in current estimates of the aerosol effects on climate, mainly due to aerosols strong temporal and spatial variation (e.g. [1]). India is one of the world's most populated countries. Along with the continuously increasing population and economic growth the increase of the anthropogenic pollutants is evident. Large emissions of aerosol and precursor gases transported from these regions can have significant impacts on air quality and climate on both regional and global scales.

In this work a measurement-based approach is applied to study the aerosol optical properties and to estimate the aerosol direct radiative effect over India. To assess this, observations from satellite instruments, such as AATSR (Along Track Scanning Radiometer onboard ENVISAT) and CALIOP (Cloud-Aerosol Lidar with Orthogonal Polarization onboard CALIPSO) are used along with a radiative transfer code. The data consists of observations between 2006 and 2010. Preliminary results show e.g. that over areas with elevated aerosol optical depths the fine particles can account for over 80% of the total aerosol extinction.

W-Sn ores of the Svetloye deposit: Mode of formation from isotope, fluid inclusion and modeling studies

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Large Svetloye W-Sn deposit (Chukotka, North-East of Russia) is located in the apical part of a leucogranite stock. The deposit is composed of a series of quartz veins among the flyschoid rocks (T 1-2), cut by the dikes (K 1). The veins are dominated by the quartz-wolframite-cassiterite-arsenopyrite-muscovite mineral assemblage. The later sulfide and quartz-fluorite-calcite assemblages are of limited development. Fluid inclusion study showed, that productive mineral association was formed by aqueous low-salinity sodium chloride fluids at T 350-270°C, P 0.5-1.0 kbar. The remarkable low salinity (<5% mass) was cryometrically found for the earliest magmatic fluids from primary magmatic fluid inclusions and fluid phase of melt inclusions in quartz from leucogranites of the stock. W and/or Sn ore formation was accompanied by increasing in alkalinity and degree of oxidation of fluids. Boiling of ore-forming fluids was rather typical of the central part of the deposit. Isotopic (H, O, Ar) study of minerals [1] and oxygen isotope zonality of host granites witness to precipitation of cassiterite-wolframite ores presumably from magmatic fluids strongly diluted with meteoric waters, interacted with wall rocks.

Analysis of possible role of main factors of W-Sn precipitation, such as cooling, boiling, interaction with wall rocks and mixing of genetically different fluids have been modelled with the help of HCh software package [2]. Natural data are best consistent with model of mixing of ore-forming solutions with exogenic fluid, reequilibrated with host rocks, as it was found for the Sn-W Iultin deposit, situated in the same ore province [3].


Strontium stable isotope variations in lunar basalts

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In the terrestrial environment strontium (Sr) stable isotopes may experience significant fractionation, both at low- and high-temperatures, involving carbonate precipitation [1] and plagioclase crystallisation [2], respectively. Recent data for lunar basalt suggests that these rocks may possess light Sr stable isotope compositions (δ88Sr = +0.16±0.07) [2] relative to mantle derived terrestrial basalts (δ88Sr = +0.30±0.07) [2,3]. However, few samples have been analysed thus far, and at the ±50 ppm precision of these measurements, obtained using an MC-ICP-MS [2,3], such variations cannot be clearly resolved.

This study presents high-precision (±10 ppm) double spike TIMs data for 87Sr/86Sr and 88Sr/86Sr for a suite of lunar basalts and anorthosites. These data confirm the light Sr stable isotope compositions observed previously for lunar rocks [2] but also demonstrate that there are significant and resolvable variations in δ88Sr ranging from +0.348 for a lunar norite to +0.151 for a high-Ti Mare basalt. These variations, taken with those for evolved terrestrial basalts, are most simply explained by the preferential incorporation of the heavy isotopes of Sr into plagioclase with a fractionation factor of ~1.0002 for 88Sr/86Sr [2]. These results clearly indicate that for the Moon primary igneous processes alone can produce significant variations in δ88Sr, without the recycling that may occur on Earth.

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129I as an oceanographic tracer in the Japan Sea

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Introduction

Iodine-129 is a natural occurring radionuclide with a half life of 15.7 Ma. During last six decades, 129I has also been released in the environment by nuclear weapons testing and the operation of nuclear fuel reprocessing plants.

The Japan Sea is a semi-enclosed marginal sea. The turnover time of water was reported about a few hundred years which was much shorter than that of the Pacific Ocean. Some of long-lived artificial radionuclides, therefore, would be useful tracers to study the oceanic circulation in the Japan Sea. In this paper, we summarize our recent studies of the Japan Sea using 129I.

Experimental

To investigate the potential of 129I as oceanographic tracer in the Japan Sea, seawater samples were collected at 7 stations by cruises of R/V Soyo-Maru and T/S Osyoro-Maru in 2007. Iodine isotopic ratios were measured by an accelerator mass spectrometry at the Mutsu Office of the Japan Atomic Energy Agency.

Results and Discussion

1. Fractions of 129I source in surface seawater were estimated using a natural isotopic ratio and fission yield. This estimation suggests that 129I in surface seawater consists of natural occurring (2%), weapons testing (10%) and reprocessing plants (88%) [1].

2. The averaged surface concentration of 129I in a subarctic circulation was higher than that in a subtropical circulation. Taking account of the location and the total amount of 129I released from reprocessing plants in EU, this different concentration would indicate that 129I released from those plants is supplied to the Japan Sea.

3. The concentration of 129I in the Japan Sea bottom water (JSBW) was higher than that of the natural level. This result indicates anthropogenic 129I is transported vertically by winter convection [2] and the turnover time of the JSBW is estimated to be about 200 years.


Selenate reduction by iron-reducing bacteria isolated from Bangladesh soil

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Introduction

Microbial reduction of highly soluble selenate and selenite to insoluble elemental selenium is an important phenomenon affecting the mobility of selenium and useful to remediation of Se-contaminated soils. Previously, we had reported the selenite reduction by Shewanella putrefaciens [1]. In this study, we examined the selenate reduction by iron-reducing bacteria isolated from Bangladesh soil.

Experimental

Soils from Samta Village, Jessore, Bangladesh were used to start an enrichment culture with H2 as a potential electron donor and Fe(III)-EDTA as a electron acceptor (Fe-medium). The enrichment was purified by serial dilution with Fe-medium. Analysis of 16S rRNA sequence of the isolate was conducted. Selenate reducing ability of the isolate was examined in an anaerobic medium containing 5 mM Na2SeO4 with a gas phase of H2-CO2 (80:20). Effect of iron on the selenate reduction was investigated in media containing 5 mM Na2SeO4 and 0-20 mM Fe(III)-EDTA. Precipitates occurred in the media were analysed by XANES spectroscopy.

Results and Discussion

An iron-reducing bacterium, designated L1, was isolated by the serial dilution. Results of 16S rRNA analysis showed that L1 is a novel species and close to Desulfitomaculum guttioideum and Clostridium celerecrescens. L1 grew in the medium with 5 mM selenate, with a gas phase of H2-CO2 (80:20). Effect of iron on the selenate reduction was investigated in media containing 5 mM Na2SeO4 and 0-20 mM Fe(III)-EDTA. Precipitates occurred in the media were analysed by XANES spectroscopy.


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Cathodoluminescence of quartz as a reflection of the evolution of the Teplice Caldera

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The late-Variscan Altenberg-Teplice Caldera (ATC) is situated in the Eastern Krušně Hory Mts./Erzgebirge on both sides of the Czech-German border. The studied borehole Mi-4, situated in the western part of the ATC, crossed all volcanic units of the caldera fill in the thickness of 950m.

According to Breiter et al. [1], the ATC consists of five volcanic phases. Two oldest units composed of the basal rhyolites (BR) and overlying dacites (DC) are calc-alkaline in character and may probably represent a product of high-degree melting of a immature material of the lower crust. Three younger units of Teplice rhyolite (TR1-3) are high-K calc-alkaline in character, significantly enriched in Rb, Th and HREE. This younger part of the ATC should be interpreted as a product of low-degree high-temperature melting of much more evolved crustal material.

The inner structure of quartz crystals was studied using cathode luminescence with hot-cathode (HC 2) and scanning luminescence (microprobe CAMECA SX100). Quartz grains from the ATC show intensive zonning in both modes of observations. The oldest unit, BR is characterized with nearly violet luminescence with weak zonning. In many cases these are just fragments of much larger grains and there are carbonate veins going through the quartz. In DC unit have quartz grains dark blue luminescence and no zonning. Quartz carbonate veins going through the quartz. In DC unit have are just fragments of much larger grains and there are violet luminescence with weak zonning. In many cases these appears as fragments only. Majority of grains were corroded individual zones could be often documented. Some grains very tiny zones symmetrically rim the core, dissolution of quartz grains from the uppermost extrusive unit, rhyolite lava (TR3) are mostly rounded (2 mm diam.), often with granophytic overgrowth.


Surface complexation evidence that amino acids prefer special sites on oxide surfaces

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Adsorption data for a variety of amino acids on rutile, amorphous titanium dioxide and hydrous ferric oxide covering wide ranges of pH, ionic strength and surface loading have been analyzed with the extended triple-layer model (ETLM), ATR-FTIR spectroscopic studies and quantum chemical approaches [1-4]. The results provide a consistent picture of the surface speciation of amino acids on oxides. The ETLM analysis requires a surface site density of 3.0 sites/nm². Each amino acid adsorbs in at least two ways to oxide surfaces: at low surface loadings, a species ‘lying down’ on the surface; at high surface loadings, a species ‘standing up’ on the surface. We focus here on glutamic acid (H2Glu) and dihydroxyphenylalanine (DOPA or H3DP) on rutile. At the highest loadings, about 0.47 sites/nm² are occupied by the ‘standing up’ Glu attached through the distal carboxylate to a surface functional group >TiO (OH²⁺). The attachment consists of one inner-sphere bond and one H-bond. The amount of Glu adsorbed corresponds to about 16% of the total site density. However, this type of attachment cannot take place on the ideal (110) face of rutile which overwhelmingly predominates on our rutile sample in SEM pictures. The reason is that groups such as >Ti (OH), or >Ti(OH)O are not present on the ideal (110) face. They are present on (111) or (101), suggesting that at least 16% of the (110) surface in our sample consists of (111) or (101) structures that contain the special functional groups that Glu prefers. A similar conclusion applies to DOPA. At high loadings, DOPA attaches to two Ti as (>TiOH²⁺)>TiHDP- with one inner-sphere bond and one H-bond from the two phenolic groups on the DOPA the separation of which (2.78 Å) almost exactly matches the two >TiOH groups (2.77 Å), but only when these are exposed on the (101) plane. Overall, the ETLM analysis indicates that both Glu and DOPA at high loadings prefer special functional groups that are not available on the ideal (110) plane, implying that most amino acid adsorption is on steps on (110) surfaces of rutile and similar structures on other oxides. HRTEM studies are underway to test this suggestion.

Trace element analysis in quartz by using laser ablation ICP-MS: A tool for deciphering magma evolution  

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Quartz is one of the most abundant minerals in the Earth's continental crust and is a common and most resistant rock-forming mineral in silica-oversaturated rocks. During post-magmatic and metamorphic alterations, trace elements are relatively stable in quartz crystal lattice. We have used laser ablation ICP-MS technique to (1) evaluate the chemical composition of igneous quartz from two comagmatic granitic and rhyolitic suites and (2) correlate cathodoluminisence internal structures and trace element patterns in quartz to define relations of element chemistry and zonation.

Internal structure of quartz grains was studied by cathodoluminscence (CL) on the electron microprobe. Trace element (Li, Be, B, Sr, Ba, Pb, Ge, Al, P, Ti, Cr, Mn) concentrations were measured using a New Wave UP-213 laser ablation system connected with sector-field single collector ICP-MS (Thermo Element 2). Laser was fired at repetition rate of 20 Hz and energy of 8-10 J/cm². All data were calibrated against the external standard NIST SRM612 glass and silica contents were used for internal standardization. Time-resolved signal data were processed using the Glitter software; caution was taken to constrain the signal to chemically homogeneous parts of the crystals and to avoid any inclusions and inhomogenities that can be potentially present in the analysed.

Our pilot samples were taken from the late-Variscan magmatic system of the A-type in eastern Krusné hory Mts. (N Bohemian Massif). The rhyolite samples from borehole Mi-4 represent evolution of the Altenberg-Teplice caldera, whereas the granite sample from borehole CS-1 document vertical zonality of the comagmatic Cínovec pluton.

Cathodoluminescence images of quartz grains (crystals and their fragments) from the rhyolite show distinct domains with a characteristic bright and dark luminescence: the cores are dark (poor in Ti, and enriched in Al and Ge), whereas rims are bright (rich in Ti and poor in Al). Quartz grains from granites are homogeneous, without any CL zonation. Evolution from the deeper protolithionite to the upper zinnwaldite granite is documented by increase of Al, Ge, B, Sr, Ba, and decrease of Ti-contents in quartz.

Computer simulation of clay mineral – biomolecule interactions  

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We show simulations of various 25-mer sequences of single stranded RNA, in bulk water and with aqueous montmorillonite clay [1]. Over timescales of only a few nanoseconds, specific RNA sequences fold to characteristic secondary structural motifs, which do not form in the corresponding bulk water simulations. Our simulations show that, in aqueous Ca²⁺ environments, RNA can tether to the clay surface through a nucleotide base leaving the 3’ end of the strand exposed, providing a mechanism for the regiospecific adsorption and elongation of RNA oligomers on clay surfaces.

We study the structural stability of three different nucleic acids, intercalated at varying degrees of hydration within a magnesium aluminum layered double hydroxide (LDH) mineral host and free in aqueous solution [2]. The nucleotides investigated are ribose nucleic acid (RNA), deoxyribose nucleic acid (DNA), and peptide nucleic acid (PNA), all in duplex form. Our simulations show that DNA has enhanced Watson-Crick hydrogen-bonding when intercalated within the LDH clay layers, compared with intercalated RNA and PNA, whilst the reverse trend is found for the nucleic-acids in bulk water. The tendency for LDH to alter the stability of the three nucleic acids persists for higher temperature and pressure conditions. These results suggest that a mineral based origin of life may have favored DNA as the information-storage biomolecule over potentially competing RNA and PNA, providing a route to modern biology from the RNA world.

Chronology of fluvial incision in the upper Ganges inferred from in situ cosmogenic isotopes

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Although past climatic cycles are well constrained, little is known about their effect on catchment erosion and sediment transport. For instance, what is the role of climate variability on river aggradation/degradation cycles in tectonically active settings? The Alaknanda River, one of the two major tributaries of the Ganges River, constitutes an ideal area for studying this question. From its glacial headwaters sourcing sediment from 7,000+ meter peaks, fueled by meltwater and the summer monsoon that annually brings the river to sustained flood levels; the Alaknanda River transports a tremendous volume of sediment to the fertile floodplain and the delta of the Ganges River. Sediment transport dynamics has fluctuated in the past with episodes of fluvial aggradation and incision. Recently, Ray and Srivastava (2010) have used OSL dating to provide a chronology of the episodic formation of river terraces, showing that it occurred during two phases: between 45 and 25 ka, and between 18 and 11 ka. A detailed knowledge of fluvial incision chronology is still lacking. Cosmogenic radionuclides (CRN) 10Be and 26Al can be used to determine how long a bedrock surface has been exposed to cosmic rays at the Earth’s surface. This can be used to quantify the timing of fluvial incision through bedrock or overlying sediments. With this aim in mind, we have collected bedrock samples along the Alaknanda River at strategic sites. Results will inform on the timing of fluvial incision in this catchment, which when combined to the chronology of river aggradation, will provide a detailed understanding of river dynamics in the lower Himalayas. By comparing these results to regional climatic records, we will be able to identify the role of climate on catchment dynamics in a tectonically active environment.


Regulation of atmospheric $p$CO$_2$ by the North Pacific Ocean since the last interglacial

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The large 80-100 ppmv variations in atmospheric $p$CO$_2$ documented in ice-cores from Antarctica over glacial-interglacial cycles provide an essential forcing mechanism in driving the climate system. Existing research on the terrestrial biosphere as well as the low latitude and Southern Oceans are capable of explaining c. 50% of this variability when invoking mechanisms including deep water upwelling, stratification and the biological pump. Evidence is presented here, using new diatom oxygen, silicon and carbon isotope data, that changes in the strength of the North West Pacific Ocean biological pump and the regional halocline also played a key role in acting as both a net sink and source of CO$_2$ between MIS 5e and MIS 4.

Methods

$\delta^{18}O$ and $\delta^{30}Si$ were analysed following a combined step-wise fluorination procedure with measurements made on a Finnigan MAT 253 with an analytical reproducibility of 0.4‰ and 0.06 ‰ respectively [1]. Diatom $\delta^{13}C$ was analysed using a Costech elemental analyser linked to an Optima mass spectrometer via cold trapping with an analytical reproducibility of 0.3‰.

Results/Discussion

Whereas the regional water column is characterised by an inefficient biological pump and significant ventilation of CO$_2$ to the atmosphere in MIS 5e, a more efficient siliceous pump during MIS 5b-c led to a reduction in such exchanges. Both intervals culminate with increased meltwater input, establishing a stratification boundary and inhibiting further productivity as well as large scale ventilation of CO$_2$. Such changes would have helped drive the climate system through the MIS 5 sub-stages and into the last glacial period.

A microbially-mediated deep terrestrial nitrogen cycle at Henderson Mine, CO

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The existence of life in deep terrestrial subsurface rocks has been established at multiple sites, yet few studies have investigated the origin of nutrients that support such life. At Henderson Mine, CO, subsurface fluids drain from boreholes at 3000’ depth, supporting a diverse microbial community based on 16S rRNA gene surveys. The fluids of several boreholes contain nitrogen in multiple oxidation states, including NH₄⁺ at 5-100 μM. Fluid mixing trends show a correlation between NH₄⁺ and degree of water-rock interaction, and so we ask whether subsurface NH₄⁺ is sourced geologically or biologically. As this Mo deposit developed from partial melting of the lower crust, it is plausible that a sedimentary source of nitrogen was mineralized into NH₄⁺, which then substituted for K⁺ in silicate minerals in the stockworks. We used FTIR microscopy to detect and quantify NH₄⁺ in from biotites and other mineral phases. We also investigate whether biological nitrogen fixation of N₂ supplies the microbial community with NH₄⁺. In the borehole fluids with the highest NH₄⁺ (~100 μM), we amplified the nifH gene from DNA extracts of filtered fluids, but not from borehole fluid DNA where NH₄⁺ concentrations were lower. We use a phylogenetic and quantitative PCR-based approach to evaluate whether nifH belongs to the novel phylum of bacteria first detected in these samples, the Henderson candidate division.

Our geochemical calculations predict that nitrification (NH₄⁺ and NO₂⁻ oxidation) is favorable in the high NH₄⁺ borehole, and so we next asked whether nitrifiers were present. The DNA from the high-NH₄⁺ borehole fluid was the only sample to contain 16S rRNA sequences from archaea and the bacterial genus Nitrospira. From this sample, we amplified the gene for archaeal ammonium oxidation, amoA, but not the bacterial version of the gene, suggesting that archaeal ammonium oxidizers (AOA) are better adapted to this environment. Finally, we amplified a novel nxrB gene encoding the beta subunit of nitrite oxidoreductase specific to nitrite-oxidizing Nitrospira. Amplification of genes for nitrogen fixation and nitrification support the existence of a subsurface nitrogen cycle. The ubiquity of Mo in enzymes of the nitrogen cycle may dictate the energy sources utilized by microbes in this subsurface Mo mine.

Is there really a mixing-zone stable carbon and oxygen isotope signal?

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A number of distinctive changes in δ¹³C and δ¹⁸O signals of carbonates in response to different diagenetic phenomena have been proposed. For example, sub-aerial exposure surfaces are typically characterized by extreme depletions in the δ¹³C and a slight enrichment in δ¹⁸O, the vadose zone is characterized by constant and depleted δ¹⁸O values, but wildly varying δ¹³C, the freshwater phreatic zone possesses negative δ¹³C values which are not so variable as the vadose zone, the mixing-zone is characterized by a co-varying trend from negative to positive δ¹³C and δ¹⁸O values, and finally the marine phreatic zone has values of both δ¹³C and δ¹⁸O which are fairly positive. In this presentation the interpretation of the co-varying trend in the mixing-zone is questioned. Instead it is proposed that this trend really represents a range of varying amounts of recrystallization taking place in the freshwater phreatic zone. The significant change in interpretation is based on observations from several deep cores in the Bahamas which have penetrated shallow-water carbonates which were deposited and sub-aerially exposed during the numerous sea-level changes during the Pleistocene. During the last glacial period sea level fell at least 120 m below its present position. Based on present interpretation of the co-varying stable C and O isotopic record at this level no freshwater water lens would have been present. Clearly a significant freshwater lens was present extending downwards as much as 40 m, coincidently corresponding to the zone of covariation between the C and O isotopes.
The Archean anorthosite-monzogranite magmatic association of the Narryer Gneiss Terrane, Western Australia

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The Narryer Gneiss Terrane is located in the Yilgarn Craton, Western Australia [1]. A layered anorthosite-gabbro-ultramafic intrusion called the Manfred Complex [2] is exposed just northeast of Mount Narryer. The complex is about 3.73 Ma old based on U-Pb zircon geochronology [3]. It is engulfed and disrupted by two banded granite gneisses. Meeberrie gneiss is mainly derived from monzogranites that have U–Pb zircon ages of 3.68–3.60 Ga [3, 4], although minor components are as old as 3.73 Ga [5]. Dugel gneiss formed from younger monzogranite to syenogranite magmas emplaced at 3.38–3.35 Ga [3, 4, 5]. Because the Manfred Complex is older than all but one component of the gneisses, it has been thought to be unrelated to the major magmatic events that produced the monzogranitic intrusions.

We have sampled additional anorthositic rocks from the Narryer Gneiss Terrane and determined their ages by LA-ICPMS U–Pb zircon geochronology. These rocks include anorthosite, leucogabbro, gabbro, amphibolite and peridotite. Anorthosites and leucogabbros located near 7 Mile Bore, north of the Jack Hills give ages of 3.73-3.63 Ga, similar to the ages for the Meeberrie gneiss, whereas northeast of Mount Dugel, north of Billabiyd well, leucogabbros formed at about 3.3 Ga, similar to ages for the Dugel gneiss. Northwest of Mount Dugel, the anorthosites formed at about 3.5 Ga; this age is similar to tonalitic to monzogranitic protoliths of the Eurada gneiss, emplaced at 3.49–3.44 Ga [5].

The correspondence of ages of anorthosites and monzogranites in the Narryer Gneiss Terrane suggests that these rocks may represent a previously unrecognized, but distinctive magmatic association of the Archean.


Most recent developments in AMS technologies

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In charge state 1+, molecular interferences can be efficiently suppressed in multiple collisions of ions with stripper gas atoms or molecules. This made a new class of AMS spectrometers possible using compact acceleration systems at terminal voltages of about 500 kV. At ETH an even more compact spectrometer was developed using a vacuum insulated high voltage platform operated at 200 kV (MICADAS). Such systems can be regarded as state-of-the-art, matching the requirements of high performance radiocarbon dating.

Recent investigations performed at ETH to explore the basic principle behind the detection technique in particular of radiocarbon at even lower energies has opened novel opportunities to further reduce size and complexity of radiocarbon detection systems. Here, the use of H as a stripper is the key to minimize energy and angular straggling in connection with charge exchange and molecule dissociation processes. Dissociation cross section of mass 14 molecules in He gas have been found to be fairly constant at energies between 40 and 100 keV and are sufficiently large to reduce the intensity of molecular beams extracted from a graphite target by 10-11 orders of magnitude. Another important fact is the high yield of charge state 1+ at energies as low as 45 keV where values of more than 75% have been observed.

In a proof-of-principle experiment, using ions at 45 keV as they are extracted from the source and a molecule dissociation unit kept at ground potential, the feasibility of radiocarbon dating measurements over the entire 14C dating range have been demonstrated.

Apart from radiocarbon, He as stripper gas has also striking advantages for other radionuclides. In particular, the detection of actinides in charge state 3+ at stripping energies of about 300 keV will become possible at unparalleled efficiencies.
The role of volcano-plutonic complex for simulation of origin of rare-metal granites from Transbaikalia, Russia

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The composition of rocks, melts (on the basis of melt inclusions study), isotopic-geochemical and geochronological characteristics (Rb-Sr and Sm-Nd isotopic systems) of rare-metal granites and accompanying sub-volcanic rocks in the ore clusters of Transbaikalia (Orlovka, Etyka, Shumilovka Li-F granites – Ta deposits, Scherlovaya Gora granites, greisen and rhyolite – Sn-W deposit, Bukuka – vein-greisen W deposit) were studied [1-3]. Close age interval of its formation, a similarity of geochemical specialization, crustal isotope-geochemical characteristics with signs of depleted of finite terms of series of differentiation allow us to consider the association of acid rock as a co-genetic volcanic-plutonic complexes. [4]. Dedicated rock types - ongonites, rhyolites, ongoryolites, trachryhyodacites – differentiates by the P-T regimes of crystallization, by the specialization of volatile, by reduction of IR Sr and, on the contrary, increasing of the series of differentiates toward depleted is reflected in a Ascertained shift of the isotopic compositions of late members differentiation and extent of mantle-crust interaction.


Kinetics of Fe-isotope exchange with pyrite at hydrothermal conditions

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The lack of data for the rates of Fe mass transfer between hydrothermal fluids and Fe-bearing minerals presents a challenge to the interpretation of subsea floor alteration processes at mid-ocean ridges (MORs). Field studies have relied on observations made from experiments performed at ambient conditions and also equilibrium theoretical models to understand the processes and mechanisms of sulfide precipitation/recrystallization [1-3]. Quantification of rates of isotopic exchange will add constraints to the chemical and isotopic evolution of hydrothermal vent fluids and minerals.

The rate of Fe-isotopic exchange between pyrite and hydrothermal fluid (FeCl₂(aq)) was examined at 350°C, 500 bars using an isotopically enriched ⁵⁷Fe tracer at pyrite saturation equilibrium. The experimental design took advantage of liquid sulfur hydrolysis to buffer redox and pH, ensuring that pyrite is the only Fe-bearing mineral in the system exchanging with the hydrothermal fluid. The degree of Fe-isotopic exchange between FeCl₂(aq)-pyrite rapidly approached ~100% within days (2.14*10⁴ mol/s). The low pH (in situ) and conditions of high dissolved sulfur may facilitate isotope exchange, as has been reported for sulfur isotope systematics [4] at similar chemical and physical conditions.

Speciation of the measured concentrations of dissolved ΣCl, ΣH₂S, ΣFe⁺⁺, ΣSO₄²⁻ and pH indicate that the fluid is saturated with respect to pyrite. Moreover, measured dissolved H₂ is in excellent agreement with that predicted from phase equilibria calculations, confirming that full equilibrium was achieved. The reaction quotient for S⁰ + H₂ ⇌ H₂S equilibrium was also determined (logK_eq~4.1).

The rapid rate of isotopic exchange between pyrite and fluid at acidic, high temperature systems, such as back-arc basins, implies that sulfide minerals may record the effects of short term temporal isotopic/chemical perturbations.

**Effects of prolonged volcanic activity of the Paraná continental flood basalts on the paleogeography, salt geochemistry and presalt oil resources of the South Atlantic rift**

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The recent discovery and intense exploration of giant oil deposits in Early Cretaceous presalt sediments of the South Atlantic rift offshore Brazil (Santos, Campos and Espírito Santo Basins), adjacent to the Paraná Continental Flood Basalt province, has thrown a new light on the complex interaction between continental flood basalts, rift evolution, and rift lake chemistry. Rifting started in the uppermost Jurassic to lowermost Cretaceous with the deposition of fluvial, fresh water lacustrine and then saline lacustrine terrigenous sediments. The continental Paraná flood basalts were dated onshore at 134.6 ± 0.6 Ma (Thiede and Vasconcellos, 2010, *Geology*), possibly related to the Valanginian Weissert Oceanic Anoxic Event. Offshore, basalt volcanism in the rift continued intermittently to 115 Ma, intercalating with presalt sediments. The flood basalts, associated with dikes, sills, and thermal uplift, blocked the entrance of sea water from the south into the southward widening rift. The main source of sediments changed from Proterozoic granites and Paleozoic sandstones to basalts. Farther out into the rift lake, terrigenous sediments gave place to the deposition of thick lacustrine limestones, dolomites, and Mg-silicates from solutions rich in Ca, Mg and silica supplied by the eroding basalts. In latest Aptian time, the entry and repeated desiccation of sea water under an arid climate led to the deposition of stratified salt, several km thick. Ca- and Mg-rich solutions from the eroding basalts, interacting with basin brines, caused the halite to be interlayered with the Ca-Mg chloride tachyhydrite. The subsequent leaching of the carbonates by CO₂ degassing from the basalts was essential to create the high-permeability oil reservoirs sealed by salt.

**Mesoarchaean suprasubduction zone ophiolite in the Tartoq Group, SW Greenland**

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The Tartoq Group comprises supracrustal rocks of dominantly volcanic origin in several discrete fault-bounded blocks. The main lithological units include: pillow lavas, dykes, gabbros, and serpentinites. Peak metamorphic conditions range from greenschist facies to upper amphibolite and lower granulite facies.

LA-ICP-MS U/Pb zircon age dating of an orthogneiss sheet that was intrusive into the supracrustal rocks yield a minimum age of 2.996 ± 0.006 Ga for the Tartoq Group.

The mafic metavolcanic rocks are dominated by tholeiitic basaltic compositions (MgO = 6-10 wt.%; and FeOT = 12-14 wt.%). They possess negative primitive mantle-normalised Nb-anomalies (NbN/LaN = 0.5-0.8). Pillow lavas, dykes and gabbros have similar flat chondrite-normalised REE patterns (LaN/SmN = 0.8-1.0), which together with serpentinite cumulate/mantle, indicate that they form a co-magmatic assemblage resembling that of an ophiolitic ocean floor sequence. La, Y, and Nb values are similar to those of modern back-arc basalts and Th/Yb vs. Nb/Yb also indicates a subduction zone component in the source of the volcanic sequence. The serpentinites have SCLM-like PGE patterns.

The structural relations combined with geochemical, and metamorphic data suggest that the Tartoq Group is a slab of Mesoarchaean suprasubduction zone oceanic crust, which after shallow subduction, was emplaced in an exhumation wedge, retrogressed by fluid input, imbricated with marginal orthogneisses, and folded and thrust into several tectonic slices and slabs with the orthogneisses.
Arsenic speciation and sequential extraction studies

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Shallow groundwater speciation studies were carried out using a field separation method in two regions of Hungary. Sequential extractions using the Tessier et al. [1] method was applied to evaluate the arsenic content distribution in each fractions. The speciation studies showed a redox environment which can promote remobilization under reductive conditions at almost each site. The sequential extractions revealed that a relatively high proportion of the arsenic could be found in the very stable residual fraction, which was also detected in other regions and by other methods (Routh and Hjelmquist [2]). At these sites the arsenic content of the groundwater was lower than at sites where the arsenic is in the more easily leachable form.

Figure 1: Distribution of arsenic in the extracted fractions versus depth.

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