

Evaluation of oxidation state and potential for bio-signatures in Fe-bearing minerals in deep-sea minerals using spectroscopic approaches

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X-ray absorption spectroscopy has proven to be a useful way of examining the chemical state of various elements in Earth materials. Iron is the most abundant redox-active element near the Earth's surface, and is particularly abundant in oceanic rocks and minerals and biological mats that occur in hydrothermal systems. Basalt is the dominant extrusive rock that comprises the ocean crust, and is approximately 10 wt % FeO, principally as Fe(II). Hydration and oxidation of basalt during water rock reactions produces clay minerals and oxides of variable composition, crystallinity, and oxidation state on the surfaces of basalt. Sulfide minerals, such as pyrite (FeS₂) that precipitate at hydrothermal vents also undergo alteration reactions that produce Fe(III) minerals. We are using XANES (X-ray absorption near-edge spectroscopy) to examine Fe-bearing rocks and minerals from the deep sea. Our objectives are two-fold: 1) test our ability to discriminate Fe(II) from Fe(III) in rocks and minerals from the seafloor; to discriminate between Fe(II) and Fe(III) we are using a new method is proposed which is usable with only ordinary levels of energy resolution, signal/noise, and energy calibration accuracy. 2) Examine the range of natural Fe(III)-bearing minerals occurring in the deep sea in order to determine if biological activity produces a distinct signature in the short- and intermediate-range order.

The Loihi Seamount microbial observatory: An extremely common deep-sea habitat for Fe-oxidizing bacteria

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Loihi Seamount is a seismically active submarine volcano that represents an emerging Hawaiian island. Hydrothermal fluids are emitted at the summit, in vicinity to the pit craters, and at more diffuse sites long the flanks of the seamount, even down to the seamount base (5000 meters). Since discovery of this seamount a prominent microbial group that has been recognized and play prominent roles in biogeochemical cycles on the seamount are the neutrophilic iron oxidizing bacteria (FeOB). FeOB habitats include the hydrothermal vents, which range in temperature from ambient (~0°C) to about 55°C presently. The composition of the fluids at Loihi is largely dictated by magmatic degassing and consequently are enriched in carbon dioxide and Fe(II) and are depleted in sulfide by comparison to other deep-seam marine hydrothermal venting habitats. Previous studies have established that FeOB play a major role in Fe oxidation and Fe oxide deposition at the site; these processes may serve as modern analogues to past major Fe oxide depositional settings. Our ongoing studies are evaluating the communities mediating Fe oxidation, the physiology of FeOB, and the biomineralogy of Fe oxides formed by FeOB. Other habitats occupied by FeOB among other microbial groups include the bare rock of the volcano itself, the olivitic basalt that undergoes hydration and oxidation reactions in the presence of oxidizing seawater, and rock that interacts with hydrothermal fluids that are being emitted. Ongoing studies are looking at the biogeochemical roles epi- and endo-lithic microbial communities play in mediating water-rock alteration reactions on basalt surfaces.

U(VI) and Eu(III) interaction with pyrite (FeS₂)

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The mechanism of U(VI) and Eu(III) interaction with pyrite was studied by solution chemistry and X-Ray Photoelectron Spectroscopy (XPS). Pyrite dissolution under anoxic conditions leads to the production of sulphoxyanions and ferrous iron, which in turn is sorbed at the pyrite surface. This sorption was confirmed by isotopic dilution. U(VI) is in competition with Fe(II) for adsorption on sulfur sites. This sorption is maximum at pH \geq 5.5. Co(II) and Eu(III) are also sorbed on pyrite surface at pH \geq 5.5, confirming that sorption on pyrite does not necessarily result from a redox reaction.

When $[U]_{\text{sorbed}}$ is below $4 \cdot 10^{-9} \text{ mol g}^{-1}$, a redox reaction occurs at the pyrite surface and leads to the formation of reduced uranium and elementary sulphur. Iron remains at oxidation degree +II during the whole process. The formation of these solid products tends to passivate the pyrite surface as the redox reaction is no longer observed when the amount of sorbed U increases. The surface is saturated for $[U]_{\text{sorbed}} = (3.4 \pm 0.8) \cdot 10^{-7} \text{ mol L}^{-1}$. The sorption at $[U] > 10^{-9} \text{ mol L}^{-1}$ can be modelled by a Langmuir isotherm with a sorption constant equal to $8 \cdot 10^7 \text{ L mol}^{-1}$.

At higher uranium (VI) concentration, a redox reaction between U(VI) and Fe(II) occurs. This reaction produces a U(IV)-U(IV) mixed (hydr)oxide, U₄O_{9(s)}, and iron (III) (hydr)oxide, such as maghemite ($\gamma\text{-Fe}_2\text{O}_{3(s)}$), which can in turn participate to U(VI) adsorption.

Comparison of estimates for Andean Plateau formation from thermochronology and stable isotope paleoaltimetry

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Quantifying the timing and rates of central Andean mountain building and plateau formation have previously been limited by (1) sparsely available age constraints on the timing of deformation, and (2) a lack of constraints on the elevation history of the plateau. We address these limitations with 52 new low-temperature thermochronometer ages, and stable isotope paleoaltimetry results of Garzzone *et al.* (2005) and Ghosh *et al.* (2006). Thermochronometer samples were collected across two 200-300 km long transects in the northern ($\sim 15^\circ\text{S}$) and southern ($\sim 19^\circ\text{S}$) Bolivia thrust belt. We assess the consistency of interpretations of plateau formation from these two approaches.

We interpreted thermochronometer cooling ages along each transect to constrain the timing of deformation in different tectonic zones across the Andes. Results suggest a consistent chronology of deformation in northern and southern Bolivia. We find: (1) deformation initiated ~ 40 Ma along the plateau margin (Eastern Cordillera) with distributed exhumation across the entire thrust belt since about ~ 15 Ma, (2) deformation in the eastern part of the thrust belt (Subandean Zone) initiated by ~ 25 -10 Ma, (3) shortening rates across each transect have been similar and decelerated over the last ~ 20 Ma, and (4) development of the Andean Plateau analogous to its modern width (but unknown elevation) occurred by ~ 20 Ma (Barnes *et al.*, 2006).

In comparison, paleoaltimetry results suggest a 3.7 ± 0.4 km increase in plateau elevation between 10.3-6.7 Ma. Plateau rise is suggested to have increased deformation in the Subandean Zone over this time interval. The retention of a dense mantle root below the plateau could account for the plateau remaining at a low elevation for ~ 10 Ma after the thermochronometer data suggest its modern width formed. However, the steadiness of shortening rates across the thrust belt since ~ 20 Ma, as well as the initiation of Subandean deformation predating plateau rise by up to ~ 10 Ma draws into the question the consistency of these two approaches. Work in progress is evaluating if temporal variations in atmospheric temperature and moisture source could account for the appearance of a low-elevation plateau prior to 10.3 Ma from stable isotope techniques.

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Multilayer fixation of dissolved phosphate on natural calcites derived from sorption experiments

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The predominance of different phosphate fixation mechanisms on natural calcite were studied in short-term batch experiments varying in hydrochemical conditions and physical properties of calcites. The fixation mechanism is crucial for the efficiency of sediment capping with calcite as an active material to reduce phosphate flux from anoxic sediments into the water column of eutrophic lakes.

Depending on the specific surface area of the applied calcite (SSA_{CC}) as well as on the dissolved phosphate concentration different processes are indicated by sorption isotherms. Low P-concentrations ($10 - 30 \mu\text{mol L}^{-1}$) in the solution together with a small SSA_{CC} ($1 - 4.3 \text{ m}^2 \text{ g}^{-1}$) lead to logarithmic shaped isotherms, indicating that adsorption processes are predominant. The same shape of isotherm can be achieved if both P-concentration ($400 \mu\text{mol L}^{-1}$) and SSA ($67 \text{ m}^2 \text{ g}^{-1}$) are high. Both cases result in a SSA_{CC}/P -ratio of 0.1 to 0.2. Low P-concentrations ($30 \mu\text{mol L}^{-1}$) in connection with a large SSA_{CC} ($67 \text{ m}^2 \text{ g}^{-1}$) as well as high P-concentrations ($100 - 200 \mu\text{mol L}^{-1}$) and low SSA_{CC} ($1 - 4.3 \text{ m}^2 \text{ g}^{-1}$) result in sigmoidal shaped isotherms. The calculated SSA_{CC}/P -ratio for both cases is > 1.8 and < 0.02 , respectively. Depending on the residual P-concentration in solution, the sigmoidal shaped isotherms can be divided into three sections indicating different processes responsible for the P-fixation on calcite surfaces. Adsorption prevails in equilibrium with lowest residual P-concentrations. The inflection of the isotherm at moderate residual P-concentrations suggests that precipitation and transformation of Ca-P-compounds becomes dominant. This is supported by characteristic Ca/P-ratios for different Ca-P-compounds, e.g. β -Tri-Calcium-Phosphate, Octa-Calcium-Phosphate. The last section, with highest residual dissolved P-concentration, shows a logarithmic form, which can be attributed to adsorption onto the newly formed Ca-P-surface. Our results indicate that the P-fixation onto calcite is as multilayer process.

In addition, calcite saturation of the solution has an implication on the precipitation process. Subsaturation leads to partial dissolution of calcite followed by heterogeneous nucleation of Ca-P-compounds whereas supersaturation is followed by precipitation via solid solution formation.

Petrography, geochemistry and isotope characteristics of authigenic carbonates from the Mid-Atlantic Ridge

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Although much work focused on sulphide mineralogy of active hydrothermal systems hosted in ultramafic rocks, little is known about the genesis of authigenic carbonates found in these settings. Serpentinization of peridotites at mid-ocean ridges leads to the formation of carbonates. The hydrolysis of peridotite minerals results in an increase in pH. The high alkalinity favours the precipitation of calcium carbonate. Almost 20% of the ocean crust consists of ultramafic rocks. The formation of carbonates in ultramafic rocks may consequently represent a major CO_2 sink in the global carbon cycle. Yet, the geochemical parameters of carbonate formation in ultramafic systems are poorly understood.

We analyzed serpentinite-hosted carbonates, sulphide-hosted carbonates, and dolomite hosted in red jasper from the Logatchev hydrothermal field. The unusual dumbbell-shaped crystal aggregates of dolomite represent the first observation of dolomite in a hydrothermal environment. From the Gakkel Ridge serpentinite-hosted carbonates have been studied. Most serpentinite-hosted carbonates are isopachous and botryoidal aragonite. Occasionally, microcrystalline aragonite is predating these cements. The paragenetic sequence of the sulphide-hosted carbonates is represented by (1) micrite, (2) botryoidal and isopachous aragonite and (3) clotted micrite. Our observations reveal that carbonate formation is not a single event during late-stage seafloor alteration. $\delta^{18}\text{O}$ values of the serpentinite-hosted carbonates range from -20.0 to $+5.3\text{‰}$, those of the sulphide-hosted carbonates range from $+1.3$ to $+4.2\text{‰}$. Dolomite in the red jasper exhibits $\delta^{18}\text{O}$ values from -9.2 to -7.0‰ . $\delta^{13}\text{C}$ values of sulphide-hosted carbonates vary from $+2.5$ to $+3.6\text{‰}$, those of dolomite dumbbells range from $+2.6$ to $+3.0\text{‰}$. $\delta^{13}\text{C}$ values of the serpentinite-hosted calcite that formed at high temperatures range from -5.8 to -5.5‰ , reflecting a signal of mantle CO_2 . The $\delta^{13}\text{C}$ values of the serpentinite-hosted aragonite range from -1.6 to $+2.7\text{‰}$, which are typical for marine carbonates. We suggest that $\delta^{13}\text{C}$ values of $+3.0\text{‰}$ and higher found for carbonates in serpentinites may reflect a partial contribution from methanogenesis. This hypothesis is supported by high Fe contents in these carbonates. Chondrite-normalized REE+Y patterns of the dolomite dumbbells are characterized by (1) a negative Ce anomaly, (2) a positive Eu anomaly, and (3) a slight enrichment of HREE. The negative Ce anomaly of the dolomite dumbbells indicates formation from oxic waters.

Denudation rates in NE-Iceland. Evolution of a steady state model of erosion

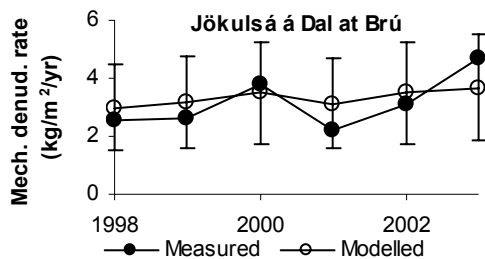
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This study critically assesses the temporal sensitivity of a steady state model of erosion that has been applied to various chemical and mechanical weathering studies worldwide. The model assumes a geochemical mass balance between the initially unweathered rock of a drainage basin and the weathering products (Gaillardet *et al.*, 1995).

The model was applied on 89 samples of river dissolved and suspended matter collected during 1998-2002 from five basaltic glacial river catchments in NE-Iceland. The steady state model of erosion was sensitive to the seasonal changes of the dissolved constituents in the rivers. However, the measured and modelled results are within the error of the method. The modelled concentrations of the suspended inorganic matter were most consistent to the measured ones, when the average annual chemical composition of the dissolved- and the suspended matter was used in the modelling (figure 1).



These results validate the use of a steady state model of erosion in estimating the denudation rate at a catchment scale. Best results are gained when samples are collected at close to average dissolved loads of the rivers.

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Dehydration processes determine fO₂ of arc and intraplate magmas

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Chromite inclusions within early-crystallised olivine phenocrysts (Fo>85 mol%) in most arc lavas have lower Fe²⁺/Fe³⁺ ratios than similar inclusions from MORB. This can be calculated to reflect a higher oxygen fugacity (ΔFMQ>+2) in the source region of arc magmas compared to the source of MORB (ΔFMQ <+1). This higher oxygen fugacity in arcs is likely related to the "subduction component" added to the asthenospheric, MOR-like mantle. Aqueous fluid by itself is a very inefficient medium to increase the mantle's oxygen fugacity, so it has been proposed that Fe³⁺-bearing melts are involved (Frost and Ballhaus, 1998). However, not all arcs show influence of a slab-derived melt.

We propose that the observed higher oxygen fugacity in arcs is related to the dehydration of serpentinites, formed in either the downgoing slab or the forearc mantle. Serpentinisation involves the hydration and oxidation of olivine and pyroxene, and generation of serpentine, magnetite, ± brucite, H₂ ± CH₄ (Frost, 1985). Serpentinites release their water into the sub-arc mantle by formation of olivine and orthopyroxene at ~2-3 GPa and 700-750°C. Olivine is always more iron-rich than its equilibrium serpentine (Evans, 2004) and neither olivine nor orthopyroxene can accommodate Fe³⁺, so ferric iron from magnetite needs to be reduced to be incorporated into these minerals. This reaction will liberate oxygen that is carried into the mantle wedge with the aqueous fluid, explaining the high oxidation state of the sub-arc mantle.

Dehydration of the similarly oxidised metabasaltic portion of the subducted slab leads to the formation of an eclogitic mineral (cpx-gt) assemblage, which does not discriminate against Fe³⁺ in the same manner as ol-opx. This material is subducted into the deep mantle, and recycled to form OIBs. This model agrees with the oxygen fugacity of OIBs being intermediate between that of MORBs and arcs.

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Biominerals, proxies, vital effects, and ocean palaeochemistry

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Successful reconstruction of the physics, chemistry and biology of past oceans from marine biominerals requires the fusion of several strands: understanding the physical basis of trace element and isotopic incorporation, modelling, empirical calibrations, analysis of natural systems, critical evaluation of the PCF, evidence by application, high resolution records, new developments. Focussing chiefly on O, C, Mg and B of planktonic and benthic foraminifera, recent work will be presented that gives insights into the biomineralisation process (vital effects), how conflicting results from proxies may be reconciled, and on changes in ocean temperature, carbonate ion saturation and hydrography over glacial-interglacial periods.

High-pressure mineral inventory in the Ries crater, Germany: A window to phase transformation processes in planetary interiors

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High-pressure mineral inventory

The impact event that created the Ries crater in the Swabian Alb 14.7 My ago induced high-pressure phase transformations in minerals in the crystalline basement. These inversions include quartz to coesite and stishovite, graphite to diamond (El Goresy *et al.*, 2001a), rutile to two new dense and ultradense polymorphs of TiO₂ (El Goresy *et al.*, 2001b; El Goresy *et al.*, 2001c). In situ study of these high-pressure polymorphs is a key method in uncovering critical parameters that promoted and controlled the high-pressure mechanisms of phase transitions, possible back transformations and in conducting a more realistic estimate of the equilibrium shock pressures in natural events.

Results and discussion

We successfully *in situ* localized quartz-coesite, graphite-diamond, and rutile to orthorhombic (space group *Pbcn*) and to the monoclinic polymorphs (space group *P2₁/c*) inversions. Quartz-coesite inversion is preferably localized at the grain boundaries to neighboring denser minerals. Raman mapping revealed the presence of coesite intergrown only with undeformed quartz thus indicating partial back inversion of coesite or plausibly complete back inversion of stishovite to quartz. Graphite/diamond inversion is never complete (<60%) and is localized exclusively at the graphite/garnet interface as a result of the high difference in shock impedance. The petrographic settings of the two new TiO₂ dense and ultradense polymorphs with their parental rutile also indicate the crucial importance of phase boundary settings in accomplishing the phase transitions. Graphite/diamond and rutile to the both dense orthorhombic and the ultradense monoclinic polymorphs are encountered in graphite-bearing garnet-cordierite-sillimanite gneisses and their coexistence allows to constrain the equilibrium shock pressures to be definitely < 28 GPa and the post-shock temperature < 200° C.

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Trace element data and fluid regime during HP-LT metamorphism of basic rocks, Ile de Groix, France

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Trace element contents in whole-rock samples and minerals of the metamorphic rocks of the Ile de Groix - part of a Hercynian HP/LT metamorphic belt - were analyzed in massive and banded eclogites and blueschists. Geochemical data indicate that the protoliths of the massive lithologies represent MORB-type basalts. The banded lithologies are of volcano-sedimentary origin.

Trace elements contents for metamorphic assemblages were determined by LA-ICP-MS. GR03 is a banded blueschist containing an assemblage of grt-ep-Fe³⁺ rich gln-pheng-rt-mt-qtz. The bulk rock incompatible element abundances in this specimen generally exceed those for its constituent minerals. Only in garnet are the HREE contents higher than in the bulk rock, reflecting the high compatibility of the HREE within the garnet crystal structure. The epidote REE contents match those for the bulk rock in the central parts of the grains and decrease rimwards. All other minerals are REE and HFSE depleted compared with the bulk rock composition. Epidote and, to a lesser extent, phengite and rutile display a positive Pb anomaly in the multi-element patterns. The bias between the whole rock and the mineral trace element patterns observed in several specimens could be explained by a fluid that only partly left the rock system during the metamorphic process and was trapped in the rock interstices (Shatsky *et al.*, 1990). It is suggested that the fluid-mineral interface processes play a crucial role during the trace element mobilization during blueschist facies metamorphism, with some blueschists representing an assemblage of metamorphic minerals and fluid components that did not completely escape the system.

The comparison of massive and banded rocks indicates that the massive rocks were less affected by the fluid/element transfer than the banded rocks. Epidote in massive eclogites is REE enriched compared to the bulk rock. The distribution of REE in epidote is highly variable in all rock types. This seems to be constrained by the local equilibrium associated with the appearance and disappearance of new stable mineral phases (garnet, apatite or titanite) during the various stages of metamorphism. We suggest that the massive rocks were less rich in fluid components before the onset of high-P metamorphism, and that during fluid escape the REE mostly remained trapped in the newly forming mineral phases.

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Diffusively driven Li isotope fractionation

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The cycling of Li at the Earth's surface results in marked isotopic fractionations (~40‰) that lead to the subduction of isotopically heavy Li. This scenario suggests that Li isotope ratios should provide a distinctive tracer of subducted components in oceanic basalts. Such promise is based on the tacit assumption of equilibrium, in which only low temperature processes can significantly fractionate stable isotopes. However, several recent experimental and observational studies have highlighted that Li isotopes are readily fractionated in magmatic processes by diffusion. In order to use Li isotopes as a tracer of recycled material it is thus critical to understand the role of diffusion on Li isotopes at different length scales.

We have examined Li isotopic profiles in phenocrysts of lava flows. Except in glassy samples, we commonly find zoned crystals. Such isotopic zoning appears to be the natural consequence of cooling, during which the partition coefficient of Li in phenocrysts increases. We have reproduced the forms of isotopic profiles in a self-consistent model driven only by cooling. Deriving absolute cooling rates depends on several parameters which are currently poorly constrained (e.g. the diffusivity of Li in olivine), but the data plausibly imply temperature drops of a few hundred degrees in hours.

The influence of diffusion on the Li isotopic composition of a whole lava flow, rather than its redistribution during final cooling, is more difficult to determine. The general over-lap of (unzoned) olivines from peridotitic xenoliths with many mantle derived melts suggest that whole rock compositions are not ubiquitously fractionated by diffusion. As an empirical assessment of possible diffusively driven differences in bulk Li isotopic compositions, we have analysed a suite of samples from the East Pacific Rise (9-10°N). These samples show near homogeneity in long-lived radiogenic isotope tracers but contrasting U-series disequilibria, suggesting their derivation from different depths of the melting regime. This should give rise to differential chemical gradients between the melts and mantle through which they finally ascend, potentially driving different diffusional loss of Li. Although the sample suite shows a significant range in $\delta^7\text{Li}$ related to disequilibrium, its magnitude is small (0.7‰), suggesting that the role of diffusion in influencing these lava compositions is minor.

Consideration of formation buffering potential and reactive mineral availability pertaining to geological storage of carbon dioxide

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One promising strategy for decreasing CO₂ emissions to the atmosphere is carbon capture and storage in deep saline formations. Modelling efforts and the experimental measurements that support these efforts are critical to determining the fate of injected CO₂. The focus of this work is CO₂-water-rock interactions as they pertain to formation buffering potential and reactive mineral availability. In addressing formation buffering potential, PHREEQC was used to model pH evolution in siliciclastic and carbonate rocks. The initial mineral and formation water compositions were determined from analyses of core samples and brines from several formations in the Alberta sedimentary basin in western Canada. Simulation parameters correspond to injection conditions of 50°C, CO₂ pressure of 100 bar and high ionic strength. The aim of this modelling is to evaluate host formation mineralogy based on the ability to buffer the acid created by CO₂ injection.

Our second goal is to better define mineral abundance and availability in siliciclastic sedimentary rocks, to support the development of relationships for upscaling reactive transport. Energy dispersive X-ray spectroscopy and back-scattered electron microscopy were used to identify minerals and characterize the spatial distributions of potentially reactive minerals in thin sections from the Alberta Basin. Minerals of mean atomic mass greater than quartz, which include those that are reactive under acidic conditions, occur as entire grains in sandstones and shaly sandstones. Kaolinite is found to cement quartz grains and line pore spaces, decreasing primary porosity and obscuring contact between pore fluids and reactive minerals. There is less kaolinite in conglomerate sandstones but reactive minerals are sparse and typically found as inclusions, thus limiting their contact with pore fluids. The sandstone specimens have between 1% and ~5% reactive minerals, but these estimates of mineral abundance overestimate the percentages of reactive minerals accessible to pore fluids by as much as a factor of five. Incorporation of these results into reactive transport models will allow for more accurate representation of formation reactivity with injected CO₂.

Reactive transport and pore-size controlled solubility in porous rocks

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Nano-scale pores in sediments and soil can modify the effective solubility of minerals, allowing highly supersaturated fluids to exist within the porous medium; this mechanism suggests that precipitation or dissolution can occur when fluid flows from small pores into larger ones, or vice versa. Pore-size controlled solubility (PCS) is a process which stems from the surface tension associated with crystals growing in rigid pores. In many ways analogous to the capillary pressure at a liquid-vapor interface within a pore, this surface tension gives rise to an excess pressure within the crystal, which can be related both to solubility and pore size. Here, we demonstrate how PCS can be incorporated into continuum equations for fluid transport and porosity evolution in simple porous media. Using numerical simulations, we demonstrate that the PCS mechanism can account for the filling of large pore spaces during transport through a heterogeneous rock matrix and represents an effective mechanism for fracture mineralization. In addition, evidence for PCS from scanning electron microscope (SEM) analyses of sedimentary rocks is also presented.

A micrometeoritic "volcanism" in the early thermosphere

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Our scenario, "EMMA" (Early Micrometeorite Accretion), describes the formation of the Earth's atmosphere through the destruction of volatile-rich micrometeorites during their frictional heating in the thermosphere [1]. We recently improved EMMA by taking into account: (i) measurements of the C, N and S contents of Antarctic micrometeorites (AMMs) [2, 3]; (ii) studies of the Wild 2 cometary grains showing that AMMs could have a cometary origin [e.g., 4]; and (iii) studies of unweathered AMMs recovered from ultra-clean snow in Central Antarctica [5].

About 99% of the AMMs are related to the volatile-rich hydrous-carbonaceous chondrites. The Earth's atmosphere has a "micrometeoritic-like" composition: the average values of D/H ratios and the Ne, N₂, H₂O and C contents of a few hundreds of AMMs are similar to that of the $\sim 2 \times 10^{24}$ grams of the Earth's atmosphere that formed about 4.4 Ga ago. This micrometeoritic "purity" of the Earth's atmosphere can be most simply interpreted if the Moon forming impact blew off most of the complex pre-lunar atmosphere at a time when the young Earth was already mostly degassed.

This similarity also suggests that the composition of the micrometeorite flux was invariant with time since the formation of the Moon. This invariance yields a simple accretion formula to estimate the total amount, M_A , of any given species, **A**, deposited on the Earth by the degassing of AMMs during their atmospheric entry after formation of the Moon:

$$M_A \sim [A(\%) / 100] \times \Phi_0$$

where, Φ_0 is the integrated mass flux of micrometeorites since the formation of the Moon, and **A**(%), the wt.% of specie **A** in AMMs. We derived three independent estimates of $\Phi_0 = \xi \times 10^{24}$ g, relying on: (i) the AMM content of either Ne ($\xi \sim 4.3$) or N ($\xi \sim 6.1$), and their total amounts in the atmosphere; (ii) the lunar cratering rates reported by W.K.Hartmann ($\xi \sim 5.6$). These three surprisingly similar ξ values yield calculated amounts of Ne, N₂, H₂O and CO₂ that actually fit their observed contents in the atmosphere within a factor of 2 to 3. The Earth's atmosphere, as well as the early Hadean climat [1], were thus likely produced by the degassing of cometary micrometeorites during the post lunar period.

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Characterization of the silicon isotopic composition of the terrestrial biogenic output from a boreal forest in Northern Sweden

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During the last decade, the potential plant impact on the biogeochemical cycle of Si via the large terrestrial biogenic Si reservoir formed by vegetation has attracted considerable interest. It has been concluded that the release of silicic acid from dissolution of soil phytoliths might exceed the Si mobilized by weathering of Si-containing primary minerals, which implies that the biogenic contribution to the total content of Si in the soil profile must be considered in weathering studies.¹

Information about Si isotopes can potentially be used for differentiation between relative contributions from biogenic and mineral sources in natural waters, soil solutions and plants. This would, however, require thorough characterization of the terrestrial biogenic Si reservoir, a task that received somewhat limited attention to date.²

The aim of the present study was to characterize the Si isotopic composition of a boreal forest, with bedrock consisting of dolomitic limestone, in Northern Sweden. Representative biomass from the forest area exhibited a surprisingly homogenous Si isotopic composition, ranging from $\delta^{29}\text{Si}$ (-0.14 ± 0.05)‰ (2 σ) to (0.13 ± 0.04) ‰. Further, a change in the Si isotopic composition of $(+0.39 \pm 0.04)$ ‰ has been detected in *Leymus arenarius*, indicating predominant accumulation of heavier isotopes from spring to autumn.

Recent studies of Si isotopic composition in plants have been focused on the root uptake of dissolved silicic acid as the only Si accumulation path. Results acquired during the present study provide compelling evidence to suggest that exogenous Si is also incorporated in the surface structure of the plant material.³ A surface contribution in excess of 5% of the total Si would introduce a significant shift in the bulk isotopic composition (>0.1 ‰) assuming that the exogenous material differed by 2‰ from the biogenic Si. This strongly suggests that the surface contribution must be carefully considered during *in situ* uptake studies.

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Intragranular replacement of chlorapatite by hydroxyapatite during scapolitisation

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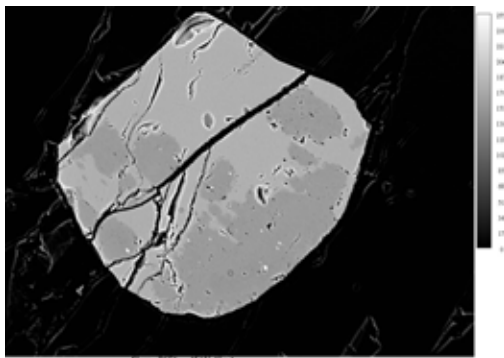
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Intragranular replacement of chlorapatite by hydroxyapatite is studied in the Ødegården metagabbro, Bamble sector of south Norway. The Ødegården metagabbro is pervasively scapolitised in a 1.5 km long zone of 50-100 m thickness, forming a rock composed of Cl-rich scapolite +rutile +apatite ±edenite ±phlogopite ±enstatite ±diopside. The magmatic apatite is non-porous and homogenous in composition with a Cl-content of c. 2 wt%. Scapolitisation transforms apatite during multi-stage replacement reactions: I) The magmatic apatite was transformed to chlorapatite with Cl-content of 6.5 wt%. II) A secondary replacement reaction transforms the chlorapatite to porous hydroxyapatite with only minor Cl (Fig. 1), and is correlated with a hydration of enstatite to talc. The observed compositional zoning in apatite is consistent with observations of apatite from pegmatites cutting the Ødegården metagabbro (Harlov *et al.* 2002). The observed changes in Cl-content of apatite is interpreted to reflect the fluid evolution and the propagation of metasomatic fronts through the gabbro. The reaction mechanism of chlorapatite to hydroxyapatite is studied by energy-filtered transmission electron microscopy (TEM). A TEM-specimen across the replacement interface was prepared using a focussed ion beam apparatus (FIB). The diffraction pattern is similar in the chlor- and hydroxyapatite parts of the crystal. The results are consistent with replacement by a coupled dissolution-reprecipitation mechanism during metasomatism.

Figure 1: Chlorapatite (light grey) partly transformed to hydroxyapatite (dark grey).



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Dissolution from a CO₂ lake

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If liquid CO₂ is stored as a dense "lake" on the deep ocean floor, it is expected to dissolve in seawater. A similar situation may occur if CO₂ is dissolved from a saturated benthic boundary layer caused by a potential leak of geological stored CO₂. Due to ocean currents and turbulence the net rate of release may increase by several orders of magnitude compared to molecular diffusion. However, density stratification induced by dissolved CO₂ will tend to reduce vertical mixing. This scenario has previously been modelled in two dimensional domain (e.g. Fer & Haugan, 2003; Haugan and Alendal, 2005). There has also been a three dimensional study (Enstad *et al.* 2006) using the MIT general circulation model (<http://mitgcm.org>). Recently the MITgcm model has been coupled with the General Ocean Turbulence Mode (<http://gotm.net/>), and this model is used to simulate the lake option. The new vertical turbulent mixing scheme takes into account density effects, and should give more realistic results for the CO₂ plume than constant eddy diffusivity models. The introduction of a third direction gives qualitatively different results for the spreading of the CO₂ plume than previous two dimensional results. Among the results we also show the hit rates of a passive tracer passing through the domain.

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Development of the high precision measurement of mercury species isotopic ratios by GC-MC-ICP-MS and its validation with two other analytical approaches

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Development of the novel technique

Mercury is transformed by microorganisms into organic forms, mainly CH₃Hg (MeHg⁺) and (CH₃)₂Hg (di-MeHg), which are highly toxic and volatile. Hence, two most abundant Hg species in the environment are Hg²⁺ and MeHg. Since gas-chromatography (GC) is one of the easiest approaches to separate this species on-line, with relatively simple sample preparation, we have estimated the suitability of the GC hyphenation with MC-ICP-MS for the precise isotopic analysis. A new protocol for the simultaneous measurement of isotopic ratios in Hg species was developed.

Validation of developed method versus other techniques

Two other analytical approaches cold-vapour generation (CVG) and continuous nebulization (CN) were chosen as reference techniques to validate the measurement of isotope ratios by GC-MC-ICP-MS. Analytical performances of these three techniques were compared, and precision for the different techniques are compared in the table below. Optimisation of the integration approach of the transient signal and GC parameters provide a suitable precision for the Hg isotopic analysis in environmental samples.

Table 1. Comparison of precision (%) for isotopic ratios of Hg²⁺ and MeHg using different sample introduction systems

	199/198	200/198	201/198	202/198
GC for MeHg ⁺	0.15	0.21	0.37	0.11
GC for Hg ²⁺	0.14	0.25	0.28	0.15
CN for MeHg ⁺	0.025	0.019	0.08	0.026
CN for Hg ²⁺	0.027	0.032	0.059	0.041
CVG for Hg ²⁺	0.032	0.051	0.14	0.098

Conclusions

When analysing real-world samples for Hg species isotopic analysis, preliminary sample preparation for both CVG and CN are very time- and labour-consuming in comparison with GC, while GC has a higher precision of the measurements. The precision of the GC-MC-ICP-MS measurement can be improved if a preconcentration step is applied before injection into the GC.

Stress-induced redistribution of Y and HREE in garnet during high-grade polymetamorphism

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Almandine garnet (Alm_{62.6}Pyr_{11.4}Sp_{8.4}And_{6.5}Grs_{4.0}) exceptionally rich in Y₂O₃ (1.8-2.3 wt%), Sc₂O₃ (0.11-0.23 wt%), HREE₂O₃ (1.9-2.3 wt%) and Na₂O (~ 0.3 wt%) occurs in Precambrian quartzofeldspathic granulites (*T* ~ 860 °C) on Hisarøya, Western Gneiss Region, Norway. The granulites were partially reequilibrated to eclogite- (*P*: 14.9 ± 1.3 kbar, *T*: 649 ± 67 °C) and amphibolite-facies assemblages during the Caledonian Orogeny. The high Y and HREE concentrations allowed quantitative analysis and imaging of element distribution at the spatial resolution of EMPA. The granulite-facies garnet is overgrown by Caledonian garnet with Y₂O₃ and HREE₂O₃ both below 0.1 wt%. The granulite-facies cores are reequilibrated to lower Y₂O₃ and HREE₂O₃ in an outer zone, typically ~ 4 µm thick, (both Y₂O₃ and HREE₂O₃ ~ 1.2 wt%), and along internal deformation structures including microfaults with horsetails, en-echelon bands and splaying features around the tip of fractures (Y₂O₃ and HREE₂O₃ ~ 1.8 wt%). Locally, the internal reequilibrated zones, typically 10-20 µm across, have shoulders with higher Y and HREE (~ 2.9 wt%) than in the original garnet, suggesting closed-system behaviour for these elements. In addition, the garnet locally displays a µm-scale complex mesh-like pattern with high and low HREE and Y bands, possibly related to straining. All features indicate ineffective Y and HREE diffusion under the present P-T conditions. Two charge-balancing mechanisms account for Y and HREE incorporation: (1) the YAG substitution involving incorporation of Al into the tetrahedral site is dominant in the granulite-facies garnet, and (2) coupled substitution with Na into the dodecahedral site is increasingly important during high-P reequilibration. The internal closed system reequilibration of the granulite-facies garnet may be due to stress concentrations build up in relict garnet during the eclogite-facies event. Possible mechanisms for reequilibration are discussed.

Petrogenesis of the basic volcanism behind the volcanic front (Cinotepeque range, El Salvador)

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Most of Quaternary volcanic activity in El Salvador is concentrated to 5 major volcanic centres, forming part of the volcanic front (VF), directly related to the subduction of the Cocos Plate under the Caribbean Plate. A volcanologically distinct volcanic province is represented by diffuse clusters of subrecent cinder cones and small shield volcanoes behind the volcanic front (BVF). While geochemistry of the prominent BVF zone, situated in the Ipala transtensional Graben along the Guatemalan–Salvadorian border, has attracted much attention, the minor Quaternary BVF field in the central El Salvador has been little studied so far. This zone of 30 individual volcanic bodies extends from the Boquerón Volcano (VF) c. 20 miles N, as far as the N–S trending horst of the Cinotepeque Range (Rapprich & Hradecký, 2005).

Compositional data available for the Cinotepeque area correspond to a suite of fairly fractionated subalkaline basalts and basaltic andesites (mg# < 55, Cr < 149 ppm and Ni < 56 ppm). Characteristic is steep increase in K₂O with increasing differentiation (SiO₂). Identical trend is observed in the lavas from Boquerón and, to some extent, the Ipala Graben (data of Carr, 2003). Similar behaviour may be demonstrated also for the other LILE. In the SiO₂–FeO^{tot}/MgO plot, the whole series falls within the Fe-rich, "tholeiitic" field. On the other hand, the K₂O increase in lavas from the more remote VF edifices is much slower and their FeO^{tot}/MgO significantly lower, typical of normal calc-alkaline rocks.

In spite of similarities of BVF and adjacent VF volcanoes, there are also differences. At the given SiO₂, the BVF lavas have higher MgO, lack the negative Eu anomaly, and show lower LILE/HFSE ratios indicative of diminishing subduction fluid involvement (Ba/La > 43). Similar pattern was reported previously also from the Ipala area.

Compositional trends in main oxides of the Cinotepeque lavas can be modelled by up to 40% fractional crystallization (plg 40%, augite 35%, olivine 20% and magnetite 6%). The enrichment in incompatible elements requires comparable degrees of fractionation. The variation in silica contents in the BVF lavas is limited. Clearly the SiO₂ content of the fractionating assemblage (43.6 %) was too similar to the most primitive lavas (49.7 %) to produce acid magmas.

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Geochemistry of an actual Fe-sulfides formation from Acisu district, Karsanti, Adana, Turkey

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The aim of this study is to elucidate the geochemical characteristics of the Acisu district actual Fe-sulfides (pyrite/marcasite) formation (Karsanti, Adana, Turkey). Around this mineralization, Upper Cretaceous ophiolite is cropped out and Paleozoic and Mesozoic aged sedimentary rocks are trusted over it. The Fe-sulfide occurrence is approximately 25 m length, 5 m width, and 3 m depth in diameter. The paragenesis comprises marcasite, chalcopyrite, quartz, hematite and calcite/dolomite. Approximately 0.5 l/s hydrothermal water (pH=4-6 and T=40-45°C) is going out to surface as a spring. Total sulfur concentration of the is 200-250 µM. It is known that Tl, Ni, Co, Mn, Zn, Pb, Ge, Cd, and As contents and Co:Ni ratio of the pyrite/marcasite are permit to distinguish them sedimentary, high and low temperature occurrences (Huston *et al*, 1995; Temur *et al*, 2006). Fe and Sb contents in the ore showed positive correlation, against to strong negative correlation of Fe and SiO₂, Al₂O₃, CaO, MgO, Sr, U. Wide ranges in concentrations of Cd, Cr, and Zn characterize the mineralization. The samples contain low Ag (12 ppm), As (26 ppm), Ni (14 ppm), Sr (1.4 ppm), Y (0.25 ppm), versus high Cu (9600 ppm), Mo (23 ppm), Pb (120 ppm), Se (86 ppm). Based on cluster analysis, four main groups can be clearly distinguished. These are **the main oxides group** (SiO₂, CaO, MgO, Al₂O₃, Sr and U) respecting enrichment of these element against to Fe; **the iron-sulfide group** (Fe, Sb, LOI and TOS) representing of the main marcasite mineralization; **the chalcophile elements group** (Zn, Cd, Hg, Ga, Ag and Cu) reflecting a mineral accumulations by sulfo-salt in solution; and the Co-Cr group (Co, Bi, Se, As, Cr, Y, and Au) representing contamination by ultramafic wall rock. On the triangular diagram of (Sb-Sr-Zn) and (Sr-Co-Zn), three mineralization types can be deviated from each other as (1) pure marcasite; (2) marcasite which contains rich lattice stoichiometric substitutions; (3) marcasite which contains rich other sulfide minerals.

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Calcification in hermatypic corals is based on direct seawater supply to the biomineralization site

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Corals are major CaCO_3 producers the ocean and their skeletons contain a unique archive of paleo-environmental information based on their isotope and trace element composition. The physiological process of biomineralization in corals, however, is not well understood, thus limiting our ability to predict their resistance to global changes, and lowering the reliability of paleo-environmental reconstructions. We investigated the biomineralization processes in the hermatypic coral species *Pocillopora damicornis* and *Stylophora pistillata* using fluorescent dyes with laser confocal microscopy. Colonies growing flatly on glass Petri dishes and small colonies completely covered with tissue (microcolonies) allowed direct in vivo microscopic observations on the actively growing crystals at the calcification site. The fluorescent cell impermeable dyes Calcein and FITC-Dextran which were added to seawater were incorporated to the aragonite skeletons of micro-colonies during short incubations of several hours. This suggests direct seawater supply into the calcification site. The seawater probably passes through the calicoblastic epithelium in narrow paracellular pathways between cells. The size of these narrow pathways is probably between 20 nm and 1 μm based on the incorporation of fluorescent plastic spheres into the growing skeleton of micro-colonies. Previous studies demonstrated the involvement of membranal Ca^{2+} channel and Ca-ATPase in the calcification process of corals. We propose that in addition to the activity of these channels and pumps, Ca^{2+} and CO_3^{2-} ions are supplied to the calcification process directly with the seawater. The activity of Ca-ATPase may be very important to elevate the pH of the seawater at the calcification site, thus increasing the CO_3^{2-} and facilitating diffusion of inorganic and respiratory $\text{CO}_2(\text{aq})$ into the calcification site. Our findings explain both the high sensitivity of corals to ocean acidification and their high fidelity in recording paleo-environmental proxies of ocean chemistry.

Environmental pollution originated from open dumping of solid waste in the cities of Eastern Black Sea

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Almost all municipalities dispose and discharge their wastes and wastewaters into the shallow sea water and the coast, mostly without treatment and outfall systems in the countries on the Black Sea coast. About 450-500 tons solid waste is generated in a day and more than 70 percent of solid waste having high organic and inorganic strength is disposed to the open dumps, land, sea and the rivers in the coastal cities of the Eastern Black Sea Region, Turkey. In the coastal cities of Eastern Black Sea Region, collection and transportation stage of solid wastes are generally well organized, but not disposal of municipal, industrial and agricultural wastes. All municipalities and industrial factories have disposed their solid wastes with together hospital and hazardous wastes to the nearest lowlands and river valley or directly into the sea environment without any prior treatment. This solid waste management strategy applied for a long time has threatened environmental health. Due to these solid waste and wastewater management strategies, coastal cities of Eastern Black Sea are faced with serious environmental and administrative challenges in recent years. In this study, an overview of the current solid waste management situation in Eastern Black Sea Region and provides a brief discussion of the future challenges are analyzed, the environmental, technical, social goals are discussed.

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Nanonuggets and their implication for core formation

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The Platinum group elements (Ru, Os, Ir, Pd, and Pt) together with Au and Re are defining the geochemical group of the highly siderophile elements (HSE) based on their 1 atm extremely high metal/silicate partition coefficients ($D^{\text{met/sil}} > 10^4$). In consequence, these elements are present in very low absolute elemental concentrations in the Earth's upper mantle ranging from 0.3 ppb for Re to 8 ppb for Pt.

However, two startling observations led to the "enigma of the overabundance of the HSE" in the Earth's upper mantle [1]. First, according to their extremely high metal/silicate partition coefficients at 1 atm, all HSEs should have been stripped entirely into the Earth's core by the Fe-rich liquid forming the Earth's core, resulting in unmeasurable low concentrations left in the mantle. Second, their elemental abundances show interelement ratios which are similar to what is observed in CI chondritic material.

The development of new analytical techniques made accurate HSE concentration determinations in basaltic, ultramafic and synthetic samples possible, and in consequence, stimulating fundamental experimental investigations of their partition behavior between metal, silicate and sulfide phases.

LA-ICP-MS techniques revealed another exciting feature of the HSE geochemical behavior: the so-called Nanonugget formation problem, mostly observed at very low oxygen fugacity conditions. At present it is under debate whether these Nanonuggets are intrinsic features of HSE solubility in silicate melts [2], contaminants [3] and, therefore, non-representative for its natural equilibrium solubility, and/or simply quench products. Including or excluding Nanonuggets during the elemental concentration determination procedure alone can account already for two to 3 orders of magnitude regarding their metal/silicate partitioning behavior. The clarification whether Nanonuggets represent the true solubility of an element, or are contaminants which, in consequence, have to be excluded from the concentration determination needs fundamental investigation.

In this paper, we present the latest results on our study on the formation and existence of Nanonuggets in Re, Os, Pt, Rh, and Ir containing experiments and discuss their influence on metal/silicate partitioning during core formation scenarios.

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Werner Schreyer's experiments on synthetic B-rich high-pressure tourmalines and micas

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Recently Werner Schreyer worked on the synthesis of B-rich mica (boromuscovite) and Al-rich tourmaline (olenite). He published many interesting papers with his colleagues, resulting from high-pressure experiments in Bochum. Olenites, where [4]B substitutes for up to ~2 apfu Si, were synthesized at PT-conditions in the range 10-40 kbar/450-700°C [1]. Like excess-B in olenite, B in boromuscovite is favoured by high pressures and low temperatures. Schreyer was also involved in investigations on natural olenite with [4]B up to ~1 apfu, from Koralpe, Austria [2-3] and from Kola Peninsula, Russia [4]. The unique pegmatite in the Koralpe, which contains B-rich olenite and muscovite may also have formed at relatively high pressures and low temperatures [5-7]. Pure endmember boromuscovite was found to be stable only at 500°C, >5 kbar and at 750°C, >10 kbar, up to 50 kbar [8]. Experimental incorporation of [4]Al extends the high-pressure stability field of boromuscovite to lower pressures [9]. We suggest a similar situation for B-rich olenite: the amount of [4]B may be pressure dependent but the stability field may be extended to lower pressures when significant amounts of [4]Al are present, as in the olenite from Koralpe. Future search for boron in muscovites and in tourmalines should be focused in high-pressure environments. Werner Schreyer's unique contributions in experimental metamorphic petrology and mineralogy together with his theoretical models should invite petrologists and mineralogists to conduct future work in this interesting field.

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Molybdenum speciation in anoxic aquatic systems: HPLC-ICPMS determination of molybdate and thiomolybdates.

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Dissolved molybdenum in fresh and marine waters is essentially under molybdate form. Though adsorbed on manganese oxides or complexed by natural organic ligands in specific conditions, molybdate is not very reactive. In anoxic condition, molybdenum can be strongly associated with colloidal organic matter [1]. When sulphide is present, transformation of molybdate to thiomolybdates ($\text{MoO}_x\text{S}_{4-x}$) has been proposed to explain Mo precipitation in euxinic water column and sediment Mo enrichment. Such pathway is validated in laboratory [2] but thiomolybdates are not yet detected in natural aquatic samples. Here we present a new method that will allow to fulfil this objective: HPLC-ICP-MS protocol is further discussed and apply to lake Pavin samples (a permanently anoxic, sulphide rich crater lake). Molybdate is separated from tetra-thiomolybdate within 15 minutes (fig 1) with optimal conditions.

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Mass independent fractionation of Hg isotopes during evaporation and condensation processes

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We measured mass independent isotope fractionation during experimental evaporation of liquid metal mercury. Recent revision of the theory of first-order mass dependent fractionation by Bigeleisen (1996) introduced nuclear field shift effects as the cause of mass independent fractionation. In equilibrium conditions, Schauble (2007) calculated the proportions of mass dependent and nuclear volume dependent isotope fractionation between several species of mercury relative to metal mercury vapour. We suggest that nuclear volume dependent isotopic fractionation can occur during evaporation and condensation of Hg.

Different sets of experiments were performed: 1) Hg liquid-vapour equilibrium between 0 and 25°C, and 2) evaporation of liquid Hg under vacuum conditions varying i- the fraction of liquid Hg evaporated at 22°C and ii- the temperature of evaporation (20°C to 100°C). Isotopic compositions were measured by generation of mercury vapour (SnCl_2) coupled with an MC-ICP-MS. For the equilibrium experiment, we report $\Delta^{202/198}\text{Hg}_{\text{liq/vap}} = 0.8 \pm 0.3\text{‰}$ (2SD) on the range of temperature. Results from the vacuum experiments fit perfectly to a Rayleigh distillation system and indicate $\alpha^{202/198}\text{Hg}_{\text{liq/vap}} = 6.5 \pm 0.3\text{‰}$ at 22°C, different from the kinetic theoretical value of 10.1‰. Isotopic fractionation between liquid and vapour Hg decreases with temperature to reach close to 0‰ at 100°C. This suggests that both kinetic and equilibrium processes are involved.

The relationship between $\delta^{202/198}\text{Hg}$ and $\delta^{199/198}\text{Hg}$ of vapour Hg in equilibrium with liquid Hg indicates that more than 90% of the total fractionation is explained by nuclear volume processes, while only 15% is required for vacuum experiments at 22°C. This proportion increases exponentially with temperature, as the importance of equilibrium increases over kinetic processes. These results suggest that liquid-vapour equilibrium isotope fractionation is mainly nuclear volume dependent, whereas kinetic fractionation is mass dependent.

Fly ashes from a waste combustor reflecting progressive Hg condensation (300°C-200°C) did not show mass independent isotope fractionation, suggesting a dominance of kinetic fractionation during Hg condensation.

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Mineralogy and alteration of fly ash from secondary Pb metallurgy

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The mineralogy and solubility of fly ash and air-pollution-control (APC) residues from a secondary lead (Pb) smelter have been studied on samples from the Příbram smelter, Czech Republic, recycling car batteries, with the emphasis on their potential environmental effect. The X-ray diffraction analysis, scanning and transmission electron microscopy and electron microprobe were used for this investigation. The presence of dominant anglesite (PbSO₄) and laurionite (Pb(OH)Cl) was observed in a sintered residue from after-burning chambers (800-1000°C). Low temperature Pb-bearing phases, such as KCl·2PbCl₂ and caracolite (Na₃Pb₂(SO₄)₃Cl), were detected in the major APC residue from bag-type fabric filters. The formation of anglesite, cotunnite (PbCl₂), (Zn,Cd)₂SnO₄ and (Sb,As)₂O₃ was observed during the sintering of this APC residue at 500°C in rotary furnace (Ettler *et al.*, 2005a).

The 720-hour leaching test on filter residues indicated rapid release of Pb and other contaminants. Caracolite and KCl·2PbCl₂ are significantly dissolved and anglesite and cotunnite form the alteration products, as was confirmed by mineralogical analysis (XRD, TEM/EDS) and PHREEQC-2 modelling (Ettler *et al.*, 2005a,b). The observed Pb-bearing chlorides have significantly higher solubility than anglesite and, following emission from the smelter stack, can readily dissolve, transferring Pb into the environmental milieu (soils, water, inhabited areas). As a result, only anglesite as an alteration product was detected by X-ray diffraction analysis in soil horizons highly contaminated by Pb smelter emissions (Ettler *et al.*, 2005c).

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Synchrotron studies of RbBr-bearing solutions ± CO₂ in synthetic fluid inclusions

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Salt- and CO₂-bearing solutions are common in geological environments, yet the consequences of interactions between these components remain unclear. XAS studies of corundum-hosted synthetic fluid inclusions that contain RbBr -CO₂-H₂O solutions have shown that: 1) Br exhibits a strong pre-edge peak in CO₂-bearing solutions at temperatures between 25 and 150°C. The pre-edge feature is similar to that shown by covalently bonded Br, but observed and calculated concentrations of covalent Br-bearing compounds (HBr, Br₂, CH₃Br) are vanishingly small. An alternative possibility is that CO₂ contributes to a charge delocalisation on the solvated Br ion that confers some covalent character to bromine-solute interactions, and; 2) Rb EXAFS at temperatures to 650°C and pressures to 0.6 GPa are consistent with a decrease in the number of waters of hydration and Rb-nearest neighbour distances with increasing temperature and pressure. This result is consistent with those of previous workers. The presence of CO₂ in concentrations of up to X(CO₂) of 0.1 is not observed to have a significant effect on either the number of nearest neighbours or ion-solute differences. However, the possibility that CO₂ affects salt speciation by inducing an increase in ion association, cannot be eliminated. Simulations show that a significant increase in the number of Rb-anion nearest number pairs would be difficult to detect by this method.

Overall, the presence of CO₂ is shown to affect the local environment of salts in solution, at least at low temperatures. Complementary methods are required to determine the magnitude and consequences of CO₂-induced changes in fluids at higher temperatures and pressures.

Non-biological fractionation of Ca isotopes in soils of the Atacama Desert, Chile

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Stable Ca isotopes hold great potential for weathering studies, but their successful interpretation will require improved understanding of processes that fractionate Ca isotopes in terrestrial surficial environments. It has been demonstrated that both biotic uptake and abiotic precipitation fractionate Ca isotopes. To consider abiotic effects in a natural context, we measured Ca stable isotope ratios ($\delta^{44/40}\text{Ca}$) in an ancient (2My), nearly abiotic, hyperarid soil in the Atacama Desert. The primary source of mobile Ca in this soil is atmospheric deposition, and the primary mechanism of isotopic fractionation appears to be precipitation of sulfate and carbonate minerals. Most of the accumulated Ca in the upper meter of this soil (2.9 kmol m^{-2}) is present as sulfates (2.5 kmol m^{-2}). Sulfate-associated $\delta^{44/40}\text{Ca}_E$ values (vs. bulk Earth) increase with depth (1.4 m) from a minimum of -1.91‰ to a maximum of +0.59‰. Linear correlation between sulfate-associated $\delta^{44/40}\text{Ca}$ and sulfate- $\delta^{34}\text{S}$ indicates a $\delta^{44/40}\text{Ca}$ fractionation factor of -0.4‰ in CaSO_4 . The overall depth trend in Ca isotopes is reproduced by a transport model that considers repeated small and infrequent rainfall events. The lowest Ca isotope values occur at shallow depths and are reproduced by a Rayleigh model, using measured soil Ca concentrations and the Ca fractionation factor predicted by the relationship with S isotopes. This indicates that the primary mechanism of fractionation in CaSO_4 is incremental and effectively irreversible precipitation with downward transport during repeated small rainfall events. This work demonstrates that significant inorganic Ca isotope fractionation in terrestrial settings can be a function of transient conditions of water supply, solution chemistry, and dissolved transport. These conditions are ubiquitous in weathering environments and should be considered in the interpretation of Ca isotope values.

Numerical modeling of continental plate retreating and crustal recycling

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Numerical experiments of oceanic subduction followed by continental collision reveal continuous subduction of the downgoing plate. When the continental plate arrive to the trench, slab pull and ridge push forces drag it into the mantle. When slab pull overcome plates coupling, the subducting plate detaches from the upper one and starts to retreat. Relatively buoyant mantle asthenosphere wedges between the two plates facilitating the continental plate retreating process. The upper crust is scraped off by the asthenosphere and thrust over the pro-foreland; on the other hand, the lower crust is dragged into the deep mantle with important consequences for crustal growth models. Models with a weak lower crust exhibit a complete delamination of the lithospheric mantle from the continental crust. At the surface, we have development of a system characterized by two different tectonic regimes: the pro-foreland is dominated by compressional tectonics, while backward crustal thinning is evidenciate by very low depth astenospheric mantle.

The Western Mediterranean formed from the Oligocene times with a mechanism supposedly analogous to our models. We try, therefore, to compare our results with an extensively studied belt of this area, the Appennines. The geological record and geophysical data show indeed interesting similarities with the models, supporting the idea that the Western Mediterranean is the result of a retreating oceanic and, ultimately, continental plate.

Mineralogy and Nd and Pb isotope signatures of clay-size fraction of northern North Atlantic sediments during the Holocene and Late Glacial: Implications for the inception of modern deep circulation pattern

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The production rate of North Atlantic Deep Water (NADW) is a critical component of the high-latitude ocean-climate system. Here we analyse the mineralogy and Sm/Nd and Pb isotope signatures of the clay-size fraction of four sediments cores collected in Labrador Sea and adjacent basins. Clay composition and their isotopic ratios bring information on the origin of particles driven by deep currents. Our aim is to monitor deep current variability through the Holocene and the Late Glacial.

The cores are located along gyres of NADW components in the NW North Atlantic. In the Iceland basin, cores MD99-2254 (2440 m deep, on the eastern side of the Bight Fracture Zone) and HU91-045-091 (3870 m deep on the western side of the Charlie Gibbs Fracture Zone) are used to document water outflow originating from the Norwegian Sea. In the Labrador and Irminger seas, cores MD99-2227 (3460 m deep, off Southern Greenland) and HU91-045-080 (3024 m deep, on the western side of the Charlie Gibbs Fracture Zone) illustrate conditions along the pathway of the Western Boundary UnderCurrent that carries NADW masses in their deep Labrador Sea gyre.

Based on sedimentary mixings of four regional end-members, our isotopic dataset emphasizes several main changes in the relative contribution of the two major components of North Atlantic Deep Water, i.e. the North East Atlantic Deep water (NEADW) and the Danmark Strait Overflow Water (DSOW) throughout the last 12 kyr, and especially during the Late Holocene.

An innovative tool for *in situ* monitoring of Fe and associated trace metal mobilization in soils

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Iron (III) oxides are common mineral components of soils, sediments, aquifers and geological materials. Trace metals associate with Fe (III) oxides as adsorbed or co-precipitated species and, consequently the biogeochemical cycles of Fe and trace metals are closely linked. Therefore, the sorption and redox chemistry of Fe (III) oxides have been widely studied because of recognition that they control water chemistry and contaminant behaviour in near-surface geochemical systems. However, most previous experimental approaches, set up to study the *in situ* evolution of such oxides through redox alternations within soils, suffered from drawbacks related to the disturbance of the soil system during the recovery of the Fe oxides.

The aim of this study was to design and test a new tool for the *in situ* monitoring of Fe and associated trace metal mobilization within soils and for tracking the potential changes of mineralogy of the Fe solid phases. Fe oxides characterized by various (i) mineralogical phases (ferrihydrite, lepidocrocite and goethite) and, (ii) associated co-precipitated trace metals (Cd or As) were directly precipitated on little (2-cm-side square) striated polymer supports. These plates were inserted both in laboratory soil columns under anaerobic conditions and, in three different soil horizons (organic-rich, albic and redoxic) belonging to a wetland located in the western part of France. The pedo-climatic setting and the hydrological and geochemical behaviour of this long-term surveyed wetland is well known. Reductive conditions allowing Fe oxides to dissolve when soils are waterlogged occur annually during the winter season.

The polymer supports were unaltered through time, suggesting that this technique can be safely used to study Fe oxide evolution. Fe amounts were quantified by XRF before and after incubation. The evolution of Fe oxides was also observed by SEM and characterized by XRD. Over a period of three months during the winter season, 69% of ferrihydrite and 15% of lepidocrocite were dissolved while the more crystallized goethite remains unaltered. SEM observation coupled with XRD showed that new iron sulphide and oxide phases precipitated on the polymer supports. Moreover, SEM observation showed that the supports were highly colonized by bacteria and biofilms suggesting that micro-organisms played a key role in the occurring mineralogical changes as well as in the Fe and associated trace metal release. Further studies dedicated to the identification of both the involved bacteria consortium and the secondary mineralogical phases as well as, kinetic study of metal release in solution will be undertaken.

Oxynitride glass-ceramic microstructures

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Oxynitride glass-ceramics attract an interest, not only because of their improved mechanical properties and refractoriness compared with oxide glass-ceramics, but also because of their presence as an intergranular microstructure in liquid phase sintered silicon nitride based ceramics. This intergranular microstructure is a result of the oxynitride liquid phase sintering medium required for densification. A tailored starting powder composition containing a combination of metal oxide and nitride additives that would form an oxynitride glass-ceramic may result in a liquid phase sintering medium that is readily crystallized after densification leaving a minimum of residual glass.

This presentation will focus on B-phase, which is a five-component phase, and its incorporation into the intergranular regions of silicon nitride ceramics. B-phase glass-ceramics may be fabricated through the nucleation and crystallization heat treatment of nitrogen rich parent sialon glasses with composition (e/o) 35R:45Si:20Al:83O:17N, where R = Er, Yb, Y or a mixture of Y and Yb. The element R determines the degree of crystallization, and it has been shown that a virtually fully crystalline, single-phase, glass-ceramic may be obtained with R = Y.

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Water diffusion in trachyte and phonolite melts

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Knowledge on water diffusivity in silicate melts is required for modelling degassing of magmas and magma/fluid interaction. Water diffusion in trachytic and phonolitic melts was investigated in a piston cylinder apparatus at pressure from 5 to 25 kbar, at 1300°C and for durations of 0 to 300 s. As starting materials we have used synthetic analogues of potassium-rich trachyte from the Phlegrean Fields, Italy and potassium-rich phonolite from Laacher See, Germany. Hydrous glasses were produced by fusion of glass powder plus water for 20 h in AuPd capsules in an internally heated pressure vessel at 1200°C and 4 kbar. In diffusion couple experiments two cylindrical halves with different water contents (nominally dry to 5.5 wt%) were combined. Water concentration profiles were measured by Fourier transform infrared microspectroscopy using the peak heights of combination bands of OH and H₂O in the near-infrared. The obtained total water profiles are asymmetric, very steep in the half with low water content but more extended into the water-rich half. Water diffusion coefficients were calculated from the total water profiles by the Boltzmann-Matano analysis and/or numerical fitting. In case of phonolite melts fitting of the profiles indicate that the water diffusivity is proportional to the total water content.

In a first experiment at 1325°C, 15 kbar for 5 min combining phonolitic halves containing 0 and 5 wt% H₂O we determined a water diffusivity of $7.7 \cdot 10^{-11}$ m²/s at 1 wt% H₂O, similar as found by Freda *et al.* [1] for trachytic melts at 10 kbar, but about 0.7 log units faster than in rhyolite (Zhang and Behrens 2000, [2]). Effects of pressure and temperature on water diffusion are discussed.

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The role of Mn oxides on the geochemical cycle of chromium: A field study in New Caledonia

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Chromium is naturally released in the environment upon weathering of ultramafic rocks containing Cr³⁺-bearing minerals [chromite FeCr₂O₄, magnetite Fe_{3-x}Cr_xO₄, olivine (Mg,Fe)_{2-x}Cr_xSiO₄ or pyroxene (Ca,Mg,Fe)_{1-x}Cr_xSiO₃]. In surface conditions, chromium occurs under two main redox states (Cr³⁺ and Cr⁶⁺), the former being much less soluble, bioavailable and toxic than the latter (Anderson, 1989). Several laboratory studies have shown that Cr³⁺ ions could be oxidized to Cr⁶⁺ ions by Mn oxides (Fendorf and Zasoski, 1992; Silvester *et al.*, 1995; Weaver and Hochella, 2003), which suggest that the concomitant occurrence of chromium and Mn oxides in soils could be hazardous. Although few field studies already addressed the question of the mobility and bioavailability of chromium in naturally Cr-enriched soils (Neel *et al.*, 2007; Garnier *et al.*, 2006; Becquer *et al.*, 2003), only one (Cooper, 2002) focused on the role of Mn oxides on these geochemical parameters.

The present study, which is supported by the french ANR-ECCO program, aims at increasing our knowledge on the actual role of Mn oxides on the geochemical cycle of chromium in soils developed upon weathering of ultramafic rocks. To reach this goal, soil samples were collected along a 60 m core drilled across a weathering sequence in New-Caledonia. Chemical and mineralogical analyses along this sequence indicate the occurrence of a saprolitic unit (ultramafic rocks more or less altered) at the bottom. This unit is overlaid by a first lateritic unit containing goethite, hematite and chromite and particularly enriched in Mn oxides (asbolan), which is itself overlaid by a second lateritic unit containing no Mn oxides. XANES analysis allowed detection of significant amounts of Cr⁶⁺ (up to 20 wt% of total chromium) in the unit containing Mn oxides whereas no oxidized chromium could be detected in the other units of the drilling core. These results strongly suggest that the reactivity of Cr³⁺ with Mn oxides observed in laboratory experiments is effective in soils and that these Mn oxides actually play a key role on the redox state of chromium, and in turn, on the geochemical cycle of this element in surface environments.

Constraining reaction rates in marine carbonate sediments using reactive transport modeling: Investigating the effects of diagenesis on Sr, Ca, and Mg

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Numerical modeling, in conjunction with pore fluid chemical and isotopic measurements, can be used to deduce mineral dissolution and precipitation rates in natural systems. The current study reports calcite recrystallization rates for a marine sedimentary section (ODP Site 807A, Ontong Java Plateau). The rates are constrained by Sr isotopes (⁸⁷Sr/⁸⁶Sr), which are sensitive at multi-million-year time scales, and Ca isotopes ($\delta^{44}\text{Ca}$), which are sensitive at time scales of tens of thousands of years. Recrystallization rates for sediments that are older than 2 Ma are ~0.2 to 2 %/Myr, which are similar to those reported in previous studies for other locations. However, reaction rates deduced for relatively young (≤ 2 Ma) carbonate sediments using Ca isotopes are significantly faster (30 to 40 %/Myr), indicating that the approximate inverse age dependence of recrystallization rate extends to carbonate sediments as young as 0.1 Ma.

Rapid rates of recrystallization in relatively young carbonate sediments have implications for the fidelity of elemental and isotopic proxies of past climate and ocean chemistry. Recrystallization may change the original elemental and/or isotopic composition of carbonate, complicating attempts at paleo-reconstructions. The current study presents model results that describe the effects of diagenesis on the Sr/Ca and Mg/Ca elemental ratios, as well as the Ca isotopic composition, of marine carbonates. Using the reaction rates constrained by Sr and Ca pore fluid geochemistry, we use numerical models to estimate that up to 25 to 30% of the initial Sr and Mg in the solid phase may be lost during diagenesis. This conclusion is different from that inferred from the Sr isotope data only. The pattern of loss is dependent on the sedimentation history, so that loss is not constant throughout the column. If there is no externally imposed advection in the sedimentary column, then Ca isotopes are not significantly modified by diagenesis. Given the upper limit of reaction rates determined at 807A, the $\delta^{44}\text{Ca}$ of the bulk carbonate sediment is altered by no more than +0.15%. The small degree of diagenetic alteration is due to the fact that Ca is a major element in calcite, as opposed to the trace constituents Sr and Mg. Finally, diagenesis is not likely to account for the fluctuations observed in the seawater Ca isotope curve over the Late Cenozoic that is derived from measurements of bulk carbonate sediments.

Geochemical records of anthropogenic change: lake sediments and peat bogs

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Radiometrically dated cores of sediments from freshwater lakes and of peat from ombrotrophic bogs have been used to reconstruct the history of heavy element deposition arising from humankind's activities over the past few thousand years. The historical records so obtained for lead, by far the most studied element, are probably the most convincing, with confidence augmented by the corroborative use of source-related stable lead isotope variations and by correspondence with independently derived records, for example from ice cores and archival herbarium mosses. Yet the bottom sediments of freshwater lakes and the living/decaying vegetation and peat of ombrotrophic bogs are dynamic systems with potential for perturbation of historical pollution records through remobilization and redistribution of elements as a consequence of inter-related physical, chemical and biological processes. The natural diagenetic enrichment of arsenic, in association with redox-sensitive iron, sometimes observed in the solid and solution phases of near-surface layers of lake sediments, and the vegetative recycling of nutrient manganese in peat bog surface plants are but two examples. Site-specific conditions, as well as element-specific processes, can be important in the case of both lakes and peat bogs and comparative studies of the two systems, where geographically possible and appropriate, may be additionally revealing. The authenticity of historical records in lake sediments and peat bogs depends also upon the accuracy of radiometric dating techniques, such as those based upon naturally occurring ^{210}Pb , nuclear fallout ^{137}Cs and ^{241}Am , and 'bomb' and cosmogenic ^{14}C , each with its own strength and weaknesses, and the current need for routine application of additional methods (e.g. ^{32}Si) with half-life (~140 y) intermediate between those of ^{210}Pb (22.3 y) and ^{14}C (5730 y).

Dynamics and internal structure of a mantle plume conduit

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Plumes are often thought of as thermal structures, the key parameter being their excess temperature with respect to the surrounding mantle, while the associated velocity field is frequently neglected. However, in order to understand the structure of a plume conduit and the internal distribution of geochemical heterogeneities we change perspective and focus on velocities and strain rates. Like the hands of an invisible sculptor, velocity gradients constantly modify the shape of heterogeneities rising in the plume conduit.

Numerical simulations of a vigorous thermal plume provide a high resolution velocity field that is used to advect deep-seated passive heterogeneities. Our first objective is to investigate the relation between initial length-scales of heterogeneities across D'' and the length- and time-scale of geochemical variations induced in the plume conduit. We also explore dynamical differences between the central and peripheral part of the plume conduit, and calculate the strain rate ϵ_{rz} , the buoyancy flux and the elongation as a function of radial distance from the plume axis. Our results clearly show that most of the plume buoyancy flux occurs in highly sheared parts of the conduit.

We then concentrate on a 'Hawaiian' plume sheared by a fast moving oceanic plate. Our fully three-dimensional numerical model allows us to study the flow trajectories inside a sheared plume conduit and the deformations undergone by passive heterogeneities. Although our approach is simplistic, we consider the lifetime of a volcano carried by the plate over different parts of the plume conduit and we investigate the relation between heterogeneous structures in the mantle and the spatio-temporal geochemical variability registered by the volcano.

Isotopic evidence for mid-Archean anoxia

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The presence of nonzero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ in the Archean and earliest Paleoproterozoic sedimentary rock record is considered to provide the strongest line of evidence for an anoxic early atmosphere. Low atmospheric oxygen is required both for production and transfer of the signal to the geologic record (Farquhar *et al.*, 2000; Farquhar and Wing, 2003, 2005; Pavlov and Kasting, 2002). Temporal trends of sulfur isotopes in the Archean record reveal periods of large amplitude non mass-dependents signals (Early and Late parts of the Archean), and others when the signal was attenuated (Middle Archean) (Ono *et al.*, 2003; Ohmoto *et al.*, 2006), and some workers argue that this interval lacks a non mass-dependent signal and records an early, transient oxygenation of Earth's atmosphere (Ohmoto *et al.*, 2006).

We have investigated this interval and present new analyses of samples from the mid-Archean record (ca. ~2.8 and ~3.0 billion years ago (Gya)) that demonstrate the presence of an unambiguous non mass-dependent signal and is inconsistent with an oxygenated mid-Archean atmosphere. Our results for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ indicate however that the character of the non mass-dependent signal is different for this interval in Earth history and provides evidence for changes in the pathways for non mass-dependent chemistry in this interval. This may reflect a change in the chemical composition of the atmosphere and may also be related to the observation of an attenuated $\Delta^{33}\text{S}$ signal at this time.

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Incipient eclogite facies metamorphism in a granulite recorded by inclusion pattern and compositional zoning in garnet

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Garnet with prograde zoning in the mesosome of a migmatitic granulite gneiss from the Moldanubian Zone, Bohemian Massif, was studied for PTt evolution using multicomponent diffusion modelling. Garnet in the leucosome has preserved an eclogite facies core, with a granulite facies rim having low Ca and high Fe, Mg and Mn. Both the mesosome and leucosome garnets show partial resorption indicated by inward zoning of Mn and variable Sm/Nd ratio at the garnet rims. Diffusion modelling of the interface between eclogite and granulite facies garnet suggests that modification of the compositional gradient occurred mostly during the granulite facies conditions, above 600-650 °C. Based on the inferred PT path, heating to the granulite facies conditions of 800 °C/2GPa with isothermal decompression to 0.8 GPa followed by cooling to 600 °C would require ~ 1.6 Ma for heating and cooling and ~ 2.4 Ma for relaxation and decompression. This corresponds to heating and cooling rate of 250 °C/Ma which was calculated for the Mn zoning in the garnet rim, and a vertical exhumation rate of ~ 1.7 cm/a. An increase of temperature to 850-900 °C for the same heating/cooling and exhumation rate would homogenize the garnet, which is the case in most felsic granulites in the Moldanubian Zone. Previous Sm-Nd dating of the prograde zoned garnets constrains their minimum crystallization age to 354 Ma, that is ca 10-20 Ma older than ages recorded by U-Pb system in zircon in felsic granulites. Recognition of two discrete metamorphic events and the calculated PTt path for the granulite may explain the compositional homogenization of garnets in felsic granulites and the reported age differences between eclogites/garnet peridotites and granulites in the Bohemian Massif.

Uptake of heavy metals, and arsenic by an aquatic plant in the vicinity of the abandoned Ervedosa tin mine (NE Portugal)

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This paper focuses on the uptake of heavy metals, and arsenic by an aquatic plant (*Ranunculus peltatus* Schrank) growing in the Tuela river in the vicinity of the abandoned tin mine of Ervedosa in the north region of Portugal. At mine, tin-bearing quartz veins with cassiterite and sulphides were exploited for tin (Sn) and arsenic trioxide (As₂O₃), until 1969. The waters at the mining site are affected by AMD, with high conductivity and significant As and metal (Co, Cu, Ni, Pb, Zn, and Cd) concentrations.

The elemental concentrations in plants were determined by ICP-MS. Water samples were analysed by GFAAS (graphit furnace AAS).

Table 1- Elemental concentrations in water and plant samples (water in µg/l and plant in mg/kg dry wt).

Samples	As	Co	Cu	Ni	Pb	Zn	Cd
1 Water	n.d.	0.56	37.1	49.1	0.60	118	0.14
1 Plant	8.47	7.96	37.6	21.1	4.46	78.6	0.40
2 Water	n.d.	0.63	38.7	23.3	13.7	225	3.15
2 Plant	6.36	18.4	103	50.8	3.10	268	13.8
3 Water	n.d.	0.60	16.2	32.5	0.71	147	1.77
3 Plant	73.8	66.7	342	108	7.56	1440	57.9
4 Water	0.30	0.64	13.3	1.78	1.65	142	0.17
4 Plant	20.2	36	156	66.5	3.43	879	31.6

The analytical data obtained (Table 1) demonstrate low pollutant concentrations in fluvial water. However, the trace elements are considerable concentrated in the plant samples. The heavy metal, and arsenic concentrations in the plants exceed the corresponding concentrations in the habitat (water) by tens of thousand times. Concentration factor (CF), as a ratio of a chemical element content in plants (C_p) to its content in the corresponding habitat (C_{ph}), was used to estimate the extent of heavy metals, and arsenic concentration by plants (CF=C_p/C_{ph}).

The plant studied can be used to decrease the heavy metals, and arsenic amounts into the aquatic environment affected by acid mine drainages. On the other hand, this aquatic plant can enter the food chains, presenting a potential danger for animal and human health.

Iron isotope variations in Holocene Baltic Sea sediments

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Sediments from the Gotland basin in the Baltic Sea display variations in their bulk Fe isotopic compositions from -0.27 ± 0.09 ‰ to $+0.21 \pm 0.08$ ‰ for $\delta^{56}\text{Fe}$ (differences in $^{56}\text{Fe}/^{54}\text{Fe}$ relative to the IRMM-14 standard). Deposits formed in freshwater with oxygenated bottom water before ~8000 years B. P. display identical Fe isotopic signatures as oxic marine sediments and igneous rocks. In contrast, samples from the more recent brackish water and periodically euxinic units have significantly lighter $\delta^{56}\text{Fe}$ values by ~0.2 ‰ on average (6 samples). Data for Fe/Al provide additional information about the cause for the shift in Fe isotopic compositions.

Enrichments in Fe/Al are characteristic for euxinic sediment deposition and can be used as a paleoredox proxy (e.g. Lyons and Severmann, 2006). Negative $\delta^{56}\text{Fe}$ values are associated with enrichments in Fe/Al in the Gotland Deep, as has also been reported from the Black Sea (Lyons and Severmann, 2006; Severmann *et al.*, 2006a), implying that negative Fe isotopic signatures could be characteristic for euxinic sediment deposition. Enrichments in Fe/Al can be explained by transport of reactive Fe from the shelf to the euxinic basin where it is transferred to the sediment by pyrite formation in the water column (e.g. Raiswell and Anderson, 2005). This is supported by pyrites with mean $\delta^{56}\text{Fe}$ values of -1.1 ± 0.2 ‰ in the Gotland Deep. Reactive Fe is derived from oxides and benthic ferrous Fe that is produced by dissimilatory iron reduction and that is suggested to be associated with negative $\delta^{56}\text{Fe}$ values (Severmann *et al.*, 2006b). Therefore, our data support the suggestion of Lyons and Severmann (2006) that Fe isotopes can be used to fingerprint the Fe enrichment process by shelf to basin shuttling of Fe. If negative Fe isotopic signatures are characteristic for euxinic sediment formation, widespread euxinia in the past might have shifted the Fe isotopic composition of the ocean towards more positive $\delta^{56}\text{Fe}$ values.

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Methane, sulfide and oxygen fluxes at methane and brine seeps of the Nile Deep Sea Fan (Eastern Mediterranean)

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The Nile deep sea fan (NDSF) of the Eastern Mediterranean hosts a huge number of active seep structures, which have only been discovered very recently. Here we have, for the first time, investigated the *in situ* benthic oxygen consumption and methane turnover at different seep systems of the eastern and central provinces of the NDSF in water depths of 1000-3000 m. The expedition BIONIL (M70/2) with RV Meteor and ROV QUEST (Marum) contributes to the DFG/BMBF Geotechnologien program MUMM and to the ESF EUROCORES project MEDIFLUX.

For our investigations several *in situ* instruments were used and combined with on board biogeochemical analyses: a microprofiler system measuring O₂, H₂S, pH and T in micrometer resolution, a benthic chamber to measure oxygen consumption and sulfide export, as well as a newly developed instrument for sulfate reduction rate measurements (INSINC). The study focused on 3 different types of seep systems – the gas emitting center of the Amon mud volcano, the mud/brine seep at the outer rim of Amon, as well as the large carbonate pavements in the central province of the NDSF characterized by low fluid flow rates.

At cold seeps, the presence of bacterial mats indicates high methane and sulfide fluxes often also linked to high oxygen consumption rates. The three systems investigated here were characterized by very different types of bacterial mats, namely a Beggiatoa type (Amon center), a Thiomargarita type (Amon flank) and an Arcobacter type (carbonate pavements). Here we compare flux rates (methane, sulfide, oxygen) as well as microbial turnover rates of these different mat communities and investigate their link to fluid flow velocity and other environmental parameters.

Geochemical characteristics of Selenium-rich silicalite formation in Ziyang, Southern Qinling, China

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A sediment formation, composed of siliceous rocks, mudstone/shale or calcs and carbonate and siltstone, has been identified for enrichment of organic matter and bacterium-alga microbe. We define this specific formation as "silicalite formation". This paper aims to study the geochemical characteristics of selenium-rich silicalite formation in Ziyang.

The study area located in the Southern Qinling of China (lower Cambrian in peripheral margins of the Yangtze Block), is known for selenium-rich in rock, and occurred serious selenium-poisoning symptom in the 1960's. Concerns on health problem and mineral resource of Se, the selenium-rich silicalite formation in this area has attracted scientific interests.

The selenium-rich siliceous rocks are important component of the Cambrian silicalite formation of Ziyang in the north of Daba region, which is characterized by hydrothermal sedimentation. Cherts are characterized by elevated concentrations of SiO₂, Se, Ba, Cu, Ni, V, As, Sb, U but lower MgO and Al₂O₃. The ratio of U/Th > 1, plots for Al-Fe-Mn and Fe-Mn-(Cu+Co+Ni) triangle diagrams, and correlations for P-Y, Zr-Cr and U-Th, all suggest hydrothermally sedimentary origin. The REE patterns show negative Ce and positive Eu anomalies. The isotopic compositions of silicon and oxygen are both similar with the hydrothermal origin. The temperature of hot water is about 78.6°C-126.20°C and suggests deep-water reservoir of siliceous rock sedimentation. The silicon-rich hydrothermal liquid contributed to enrichment of selenium in the study area.

In conclusion, further study of the forming environment and metallogenic characteristics of the selenium-rich silicalite formation is of great significance for both Se-related ore minerals and health interests.

Acknowledgment

This study is supported by NSF of China (40673029).

$\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ excursions in the post-glacial Sinian to Early Cambrian interval in Guizhou, South China

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The investigated area is located on the southeast border of the Yangtze platform. Five lithostratigraphic units are recognized in ascending order: the Nantuo (NT), Doushantuo (DST), Dengying (DY), Gezhongwu (GZW) and Niutitang (NTT) formations. The DST Fm overlies conformably on the NT Fm characterized by glaciogenic diamictite. In the basal part of the DST Fm is a ~4 m thick dolostone bed (so called cap carbonate). Upon this bed is the main part of the DST Formation dominated by phosphorite intercalated with dolostone and dolomitic pelite. The overlying DY Fm is composed of pure dolostone, followed by another set of phosphorite deposits called the GZW Fm. The GZW Fm is rich in small shelly fossils of Cambrian age, and covered by the NT Fm, a set of black shales with copious sponge fossils.

The values of $\delta^{13}\text{C}_{\text{carb}}$ show a wide range from -6.20‰ to 4.00‰, roughly consistent with that illustrated by Jacobsen & Kaufman (1999) for the same interval. The $\delta^{13}\text{C}_{\text{carb}}$ curve starts with a moderate positive shift after the glaciogenic diamictite and then goes into a negative shift, which persists up to the boundary between the DST Fm and the DY Fm. The second positive shift of $\delta^{13}\text{C}_{\text{carb}}$ occurs within the DY Fm, followed by another negative shift in the GZW and NTT formations. The values of $\delta^{13}\text{C}_{\text{org}}$ vary from -21.99‰ to -33.58‰, leading to a maximum oscillatory amplitude of 11.59‰. Being similar to the $\delta^{13}\text{C}_{\text{carb}}$ curve in shape, the $\delta^{13}\text{C}_{\text{org}}$ curve also demonstrates two positive shifts in the NT Fm and the DY Fm, and two negative shifts in the DST Fm and the interval from the GZW Fm to the NTT Fm.

Some studies have provided paired analyses of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$. Hollander & McKenzie (1991) show that the temporal carbon-isotopic curves of calcite and particulate organic carbon in a modern eutrophic lake correlate with each other to some extent, and the carbon-isotopic difference ($\Delta B = \delta^{13}\text{C}_{\text{poc-calcite}}$) indicating the effect of photosynthetic isotopic fractionation increases in response to increasing concentration of dissolved carbon dioxide ($\text{CO}_{2(\text{aq})}$). However, the timing of the peaks or valleys of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ curves may not always coincide due to other factors besides photosynthesis, which complicates the use of ΔB for evaluating the relative variations of $\text{CO}_{2(\text{aq})}$ with geologic time (Kump *et al.*, 1999). In our study, the coincidence of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ profiles suggests a dominating effect of photosynthesis on carbon-isotopic discrimination. Thus ΔB may be useful to understanding the relative changes of $\text{CO}_{2(\text{aq})}$ that may have occurred in the investigated area during the post-glacial Sinian and the Early Cambrian. This work was supported by NSFC (Grant Nos. 40472014 and 40572017).

Cosmogenic $^{21}\text{Ne}/^3\text{He}$ in olivines and pyroxenes from a Pleistocene basalt flow, western Grand Canyon National Park, Arizona, USA

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The Bar Ten lava flow is a Pleistocene basalt flow located in the western margin of the Uinkaret Volcanic Field in Grand Canyon National Park (AZ, USA). It was chosen as a calibration site for the production of cosmogenic ^3He and ^{21}Ne ($^3\text{He}_c$ and $^{21}\text{Ne}_c$) because it has more than 600 m of relief and has negligible erosion due to a regional desert climate. Together with other calibration sites of CRONUS-EU, it was selected to evaluate how production rates are affected by changes in altitude and latitude. The lava flow erupted between 60 and 150 ka based on two $^{40}\text{Ar}/^{39}\text{Ar}$ and one thermoluminescence ages. Low K content, excess Ar, and abundant glass in this basalt flow have made it difficult to obtain more accurate ages. Cosmogenic samples were collected from stable primary surfaces at elevations of 1180 to 1820 m along a vertical transect between 36.2239 and 36.2417° N. He, Ne, and Ar were analyzed by step-heating of olivine and pyroxene separates and $^3\text{He}_c$ and $^{21}\text{Ne}_c$ components have been determined. We evaluated $^{21}\text{Ne}_c/^3\text{He}_c$ values, assuming that eruption age and erosion should have no effect on the ratio, if $^3\text{He}_c$ and $^{21}\text{Ne}_c$ are produced at constant rates relative to each other. $^{21}\text{Ne}_c/^3\text{He}_c$ varies from 0.19-0.20 for pyroxenes and from 0.35-0.39 for olivines. The difference between mineral phases may be due to differences in mineral composition affecting production of $^{21}\text{Ne}_c$; production of $^3\text{He}_c$ is less sensitive to variations in mineral composition. Olivines in our study contain 26-27 wt.% Mg, whereas pyroxenes contain 9-11 wt.% Mg. Lower Mg content decreases the production of $^{21}\text{Ne}_c$ and thus lowers the $^{21}\text{Ne}_c/^3\text{He}_c$ value for pyroxenes compared to that of olivines. Production rates based on elemental composition or on published calibrated values were scaled to our specific field site using several scaling methods. These production rates yield cosmogenic ages that are bracketed by the $^{40}\text{Ar}/^{39}\text{Ar}$ and thermoluminescence ages, but the independent dating techniques are thus far not accurate enough to specify which production rate and which scaling method is best suited for this calibration site.

Comparison of thermodynamic data for aqueous species with focus on hyperalkaline conditions

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Introduction and objective

Presently, geochemical databases lack agreement on thermodynamic properties for a substantial number of aqueous species and minerals. Some discussion of thermodynamic data can be found in the literature for minerals and solid phases (e.g. Arthur *et al.*, 2005), but not much attention has been paid to aqueous species.

The objective of this study is to address the thermodynamic properties of aqueous species with emphasis on major components relevant for hyperalkaline conditions. For this purpose, the most commonly used and accessible thermodynamic databases have been treated in similar fashion. Six databases were included: llnl-EQ3/6, minteq, phreeqc, wateq4f, JAEA and NAPSI.

Method and results

Pertinent temperature dependent thermodynamic data for 66 aqueous species were evaluated. The equilibrium constant for species association ($\log K$ at 25 °C), ΔH_R and the temperature dependence of $\log K$ (analytical expressions where available) were taken for each species and each database. The data bases were first brought to a common format in terms of basis species. Results for $\log K$ up to either 100 °C or 300 °C (extrapolated by Van't Hoff, or given by analytic expressions) were graphically compared relative to the value at 25 °C, and in absolute terms. Select literature sources and the HKF/SUPCRT model were used in addition to try and resolve some of the discrepancies.

Discussion

The results point at some obvious shortcomings, limitations and discrepancies, but some of the interpretation is limited by the absence of an absolute reference. Modelling calculations on alkaline systems using different databases and including select solid phases are recommended for a more practical comparison, and this work is currently in progress.

This research project is associated with the Grimsel Test Site (CH) and supported by Nagra (CH), POSIVA (SF) and JAEA (JP).

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Passivating layer formation during glauconite dissolution: implications for mineral sequestration of CO₂

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The kinetic of glauconite dissolution in the pH range from 2 to 10 (T= 25°C) has been determined from flow-batch reactor experiments. The textural and microstructural aspects induced by the dissolution process have also been characterized by XRD, HREM and BET. As a result of this analysis it is shown that, in acid conditions, glauconite is slightly more soluble than other silicates ubiquitous in sediments. The dissolution mechanism is incongruent at very acid pH values and tends to be congruent for intermediate and neutral values. Microstructural analysis show that kinetic factors are strongly influenced by structural factors. Dissolution of glauconite takes place in two steps involving, first, the disorder of tetrahedral and octahedral layers and, second, the release of cations to the solution, this process being controlled by the rate of liberation of the interlayer cation (K⁺). As a consequence, an amorphous phase is formed that evolves compositionally to a more silica-rich end-member. The reactive surface is reduced during this process, giving rise to the formation of a passivating layer that has considerable influence on the dissolution rate. These experimental results have been used to analyze, by geochemical modelling, the response of glauconitic sediments during carbonation reactions.

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The replacement of gypsum by CaCO_3 polymorphs: Reaction steps and formation of pseudomorphs

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On the Earth's surface, the replacement of evaporitic calcium sulphates (anhydrite and gypsum) by CaCO_3 is a common phenomenon that can lead to the formation of large deposits of diagenetic carbonates. In spite of the geological and industrial implications of this phenomenon, very few experimental studies have been conducted to investigate the microscopic mechanisms involved in this replacement process. Here we present an experimental study of the interaction between gypsum and carbonate-bearing aqueous solutions. This interaction leads to the replacement of gypsum single crystals ($\sim 3 \text{ mm}^3$) by an aggregate of CaCO_3 crystals. Scanning Electron Microscopy (SEM) and glancing incidence X-ray diffraction (GIXRD) were used to monitor the development of the replacement process. The replacement takes place through a number of solvent-mediated transformations, which involves the dissolution of gypsum and the sequential formation and dissolution of different CaCO_3 polymorphs. Although the actual sequence of reactions depends on the initial concentration of carbonate, amorphous calcium carbonate (ACC) is always the first phase that forms and can be considered a precursor for the formation of more stable crystalline CaCO_3 polymorphs. Moreover, the initial concentration of carbonate also controls the kinetics of the replacement and the degree of faithfulness of the pseudomorphs. The phase formation sequence and the textural characteristics of the replacement are interpreted on the basis of the evolution of physicochemical parameters, like the supersaturation with respect to the different CaCO_3 polymorphs and the $[\text{SO}_4^{2-}]/[\text{CO}_3^{2-}]$ ratio in the aqueous solution.

From crystals to clusters: A molecular simulation study of CaCO_3 configurations

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Equilibrium relationships involving solids are based in bulk thermodynamic properties that concern ideal crystals of infinite size. However, real processes towards equilibrium imply development of finite molecular-scale entities. The configuration of these early-stage clusters and the estimation of their excess energies with respect to the ideal crystal is key to understand the macroscopic behaviour of a given system. Here, starting from the ideal atomic positions in calcite, aragonite, or vaterite, the relaxation in vacuum of finite clusters of CaCO_3 has been explored. With the aim of determining the influence of the cluster size on its energy and on its geometrical configuration, a series of CaCO_3 clusters have been simulated and their lattice energies calculated. The cluster geometry has been fully optimized at constant pressure and its energy has been determined using GULP. A wide variety of clusters ranging from 1 to 2000 formulae has been considered for each (calcite, aragonite, or vaterite) starting structure. GULP calculations have been carried out using the pair potentials set derived by Rhol *et al.* (2003). In a number of cases the final configuration has been checked with good agreement using the DFT code SIESTA (Soler *et al.*, 2002). Although these simulations represent not fully realistic scenarios, some results are relevant from the point of view of the polymorphic precipitation of CaCO_3 . A fundamental question like the size that must have a cluster to be considered calcite, aragonite, or vaterite is addressed from the diffraction patterns of the relaxed clusters.

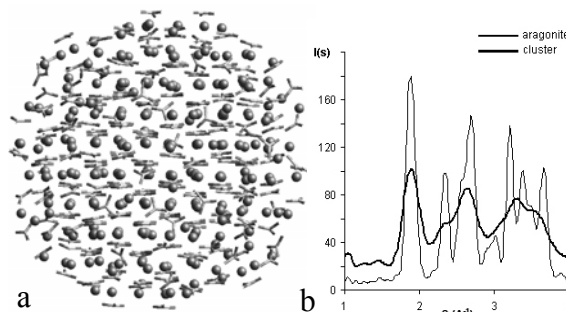


Figure 1: relaxed aragonite cluster with 250 formulae (a) and calculated diffraction patterns (b).

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Mapping petrographic variations with gamma spectrometry in granites: The example of the Três Córregos Granitic Complex, SE Brazil

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Two large Neoproterozoic bodies, the Cunhaporanga and Três Córregos Granitic complexes (CGC, TCGC) crop out in Paraná state, SE Brazil, constituted mainly by calc-alkaline granitoids. Both show ellipsoidal outlines, with a NE orientation, the prevailing basement structural trend in SE Brazil. CGC shows poor outcrop pattern and a large faciological diversity, not so TCGC. Aerial gamma spectrometric surveys were used to test variations in K, U, Th abundances for definition of facies domains in both complexes. Colorgraded maps were prepared for TC, the three elements and several calculated factors (including U/Th, U/K, Th/K ratios, F factor, triangular K-U-Th, etc.). In the case of TCGC, the color maps clearly reproduce the petrographic distribution pattern established during ground mapping. Aerial gamma spectrometry showed, for TCGC, the potential for accurately pinpointing petrographic variations.

Melt supply and magmatic evolution at a large central MOR volcano located in the Lucky Strike Segment

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New major and trace element, volatile (H₂O and CO₂) and Sr-Nd-Pb isotopic, data on samples from the Lucky Strike segment (LSS) are presented. All studied samples are E-MORBs, but different degrees of enrichment are identified. LSS basalts have been subdivided into three distinct compositional groups: In Group 1, the basalts have the highest more-to-less incompatible element ratios (e.g. La/Sm, Nb/Zr, Ba/Y) and have the most Sr-Nd-Pb radiogenic values. They are spatially restricted to the central part of the axial volcano, are highly vesicular, and plagioclase phyric. Group 3 basalts have the lowest more-to-less incompatible element ratios and the lowest Sr-Nd-Pb radiogenic values. They were collected throughout the LSS (from 37°12,0' to 37°27,3' in latitude), are almost aphyric and exhibit low vesicularity. Group 2 basalts have chemical characteristics intermediate between those of Groups 1 and 3. This subdivision is readily recognised in the volatiles data. Group 1 glasses have higher dissolved H₂O concentrations (and estimated pre-eruptive CO₂ concentrations), relative to those of Group 3, but have lower H₂O/Ce ratios (108-197 and 251-343 for Groups 1 and 3, respectively) that are well below the average defined for this MAR region (253±33).

Taking into account the sample spatial distribution, the bathymetric (shallow depths at segment centre), and the gravity data (negative "bull's eyes" RMBA anomalies at segment midpoint), together with the geochemical data interpretation, a genetic volcanic model is generated. The enriched, more fertile, mantle heterogeneities (Group 1), related to Azores mantle plume material, in the LSS sub-oceanic mantle, are delivered to the centre of the segment by highly focused, sub-lithospheric processes. Forming wetter domains, they start to melt first, deeper in the mantle, melting more, but generating lower melt fractions, than the ambient mantle (Group 3). Group 1 vesiculating melts, having their density reduced, will be aggregated in a high-level axial magma chamber (AMC). The limit of neutral buoyancy of these magmas is never reached, thus the magmas are delivered vertically to the segment centre. Further magmas, formed from melting of the ambient mantle, will be aggregated in the AMC. Thus, initial mixing of Group 1 and 3 melts and, lastly, only differentiation of Group 3 melts will produce Group 2 and 3 basalts, respectively. The disruption of pressure equilibrium of the magmatic system as a result of the ridge extensional stress regime, and the subsequent magnitude of internal overpressure in the magma reservoir will control the magma delivery along the LSS.

C₃₂ N-Alkan-1-ol as specific indicator of C₄ tropical plants in marine sediments

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Contents, distribution patterns and molecular stable carbon isotope composition of these compounds have been studied as markers of continental vegetation over the last 320 kyr in a set of samples from the tropical Indian Ocean core MD98-2165 (9°38'96S, 118°20'31E, 2100 m).

The concentration changes of these compounds show a general pattern dominated by the well defined glacial-interglacial oscillation. Eolian inputs were much stronger during the glacial periods. The *n*-alkanes range between C₂₃ and C₃₃ and are characterised by high odd-over-even carbon number preference and predominance of the C₃₁ *n*-alkane, whereas the *n*-alkanols range between C₂₀ and C₃₂ and are dominated by even-over-odd carbon numbers with maxima at C₂₈ or C₃₂ *n*-alkanol. In this respect, warmer and wetter conditions appear to favour deposition and preservation of the C₃₀ homologue and colder and drier conditions favour the C₂₈ *n*-alkanol. However, the C₃₂ *n*-alkanol becomes an additional major homologue during the glacial times, suggesting an expansion of C₄ plants during these arid conditions as reported by Rommerskirchen (2006). The stable carbon isotope weighted mean average of the *n*-alkanes (*n*-C₂₇ to *n*-C₃₃) fall in the range between -30.5 and -34.5‰, typical of leaf-wax *n*-alkanes biosynthesised by C₃ plants. The lower δ¹³C values are observed during warm and humid interglacial periods, when the estimated C₄ plants contribution decreased ~15 wt %. This is consistent with the negative relationship existent between δ¹³C of C₃ plants and water availability (Liu *et al.*, 2005). The weighted mean average δ¹³C values of *n*-alkanols (C₂₀-C₃₂) fall in the range between -24.4 and -32.6‰, again with lower δ¹³C values during interglacials. Amazingly, the δ¹³C of C₃₂ *n*-alkanol reveals a clear C₄ plant signature during cold and dry conditions. These results demonstrate that *n*-alkanes and *n*-alkanols, but most particularly the C₃₂ *n*-alkanol, show a distinct pattern of contributions from C₄ plants to marine sediments during arid conditions and therefore, they can be used as indirect proxy of continental climate conditions in the tropics.

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Chemical weathering rates inferred from cosmogenic radionuclides and immobile element enrichment: Measurements in the Idaho Batholith

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Chemical weathering regulates many biogeochemical and Earth surface processes. It nourishes ecosystems by supplying nutrients to natural waters, promotes physical erosion by weakening bedrock, and buffers Earth's climate over geologic time by modulating atmospheric carbon dioxide concentrations. Long-term measurements of chemical weathering rates (and of their dependence on external factors such as climate) are thus important for understanding the biogeochemical and geomorphological evolution of the Earth's surface, and for quantifying the recent impact of humans on the environment. Chemical weathering fluxes can be measured in mountainous terrain using cosmogenic radionuclide measurements of long-term denudation rates, coupled with measurements of the rock-to-soil enrichment of chemically inert tracers (Kirchner *et al.*, 1997; Riebe *et al.*, 2001; Riebe *et al.*, 2003). This technique has two major strengths: (1) it can be applied to a wide range of actively eroding landscapes, whereas other methods typically require non-eroding, datable soils, and (2) it intrinsically averages over the long timescales of soil formation and denudation (typically 1000-100,000 years in soil-mantled hillslopes), and thus sheds light on landscape evolution processes. Here we use this method to measure chemical weathering fluxes along an altitudinal transect on Pilot Peak. This transect spans 1500 meters of altitude in the granitic Idaho Batholith, USA, and thus spans ~10 °C in mean annual temperature. Pilot Peak is unglaciated, exhibits little variability in bedrock mineralogy, and is mantled with well-mixed soil at all elevations. Our preliminary data suggest that rates of chemical weathering, as a function of total denudation rates, are not a strong function of elevation, and hence not a strong function of temperature. These results also imply that chemical weathering fluxes account for less than 20% of the total denudation flux at Pilot Peak, and thus point toward the dominance of physical processes over chemical processes in sculpting this landscape.

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Revealing the importance of endospores in sediments

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Introduction

Endospores are bacterial resting stages being able to remain viable for long periods of time. Consequently, they can be expected to accumulate in sediments during burial and may contribute significantly to total cell counts. This emphasises the need for a new cultivation-independent approach for the quantification of bacterial endospores in sediments.

Application of dipicolinic acid for estimation of endospore numbers

In the present study, dipicolinic acid (DPA), a biomarker for endospores, was used to quantify endospores in sediment samples. Sediment cores of about 6 m length were collected from different sites in the backbarrier tidal flat of the island of Spiekeroog in the southern North Sea and analysed for their DPA content to determine endospore depth profiles. For conversion of sediment DPA contents into spore numbers, purified endospores of tidal flat strains were investigated for their DPA content.

Contribution of endospores to total cell counts

Sediment samples taken from different lithological subunits of the cores showed high variations in DPA contents. Estimated spore numbers were in a range of 10^5 to 10^7 endospores g^{-1} sediment and accounted for up to 10% of total cell counts. Huge differences in endospore numbers estimated from DPA contents and determined by viable counts obtained after pasteurization (Köpke *et al.*, 2005) were found. The conversion of sediment DPA contents resulted in at least three orders of magnitude higher endospore numbers than the most probable number (MPN) counts.

Conclusions

Since quantification of endospores on the basis of DPA content does neither discriminate between viable and non-viable spores nor between different physiological groups, it apparently provides a more realistic estimate of endospores as part of the microbial community than cultivation-dependent approaches. For this reason, we suggest to use DPA for the determination of endospore numbers in addition to total cell counts in order to reveal the importance of endospores in sedimentary microbial communities.

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New approaches for the analysis of stable and radiogenic strontium isotopes using LA-MC-ICP-MS

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Strontium isotopes in various marine carbonates have been determined using an "AXIOM" MC-ICP-MS in combination with a NewWave UP193 laser ablation unit. Using new developed measurement protocols we did achieve an external reproducibility of Sr^{87}/Sr^{86} ratios in carbonates of about 18 ppm (RSD). For recent and sub-recent marine carbonates a radiogenic strontium isotope ratio Sr^{87}/Sr^{86} of 0.70917(1) was determined, which agrees well with the accepted value for modern sea water. It was achieved without the use of any additional correction of the data. Only the rubidium correction was performed in its accepted form and the strontium isotope ratios were normalized to a Sr^{86}/Sr^{88} ratio of 0.1194 using the exponential law for fractionation correction.

A major benefit of the applied method is the direct determination of the stable strontium isotope fractionation. Assuming stable plasma conditions and a reproducible sample ablation this method is advantageous when compared to "conventional" MC-ICP-MS. It avoids additional fractionation of the sample strontium due to the chemical pretreatment (ion chromatography and solution preparation).

In aragonitic sclerosponge samples the stable strontium isotope fractionation was determined via LA-MC-ICP-MS. In these samples, spanning a temperature range of about 11°C, stable strontium isotope fractionation was found to be temperature dependent. The Sr^{88}/Sr^{86} was positively correlated to temperature. The latter correlation was estimated to 0.0396(103) per mill/°C. This value agrees within the analytical uncertainty with previous findings for coralline aragonite of 0.033(5) per mill/°C (Fietzke & Eisenhauer, 2006).

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The evolution of the Ediacaran sulfur cycle: A paired sulfate-pyrite $\delta^{34}\text{S}$ approach

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An anomalous enrichment in marine sulfate $\delta^{34}\text{S}_{\text{SO}_4}$ is preserved in globally-distributed latest Ediacaran – early Cambrian strata. The proximity of this anomaly to the Ediacaran-Cambrian boundary and the associated evolutionary radiation has invited speculation that the two are causally related. Here we present a high resolution record of paired sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$) and pyrite ($\delta^{34}\text{S}_{\text{pyr}}$) from sediments of the Ara Group, Sultanate of Oman. An enrichment in $\delta^{34}\text{S}_{\text{pyr}}$ coincides with the interval of enriched $\delta^{34}\text{S}_{\text{SO}_4}$, beginning at ca. 550 million years ago (Ma) and continuing through at least ca. 540 Ma. These data are evaluated using a new approach based on paired $\delta^{34}\text{S}_{\text{SO}_4}$ - $\delta^{34}\text{S}_{\text{pyr}}$ data that enables us to calculate both $\delta^{34}\text{S}_{\text{in}}$, the isotopic composition of the sulfur flux entering the ocean, and f_{pyr} , the fraction of sulfur buried as pyrite. It appears that basal Ediacaran $\delta^{34}\text{S}_{\text{in}}$ was significantly enriched beyond bulk Earth composition and became progressively more enriched through at least the earliest Cambrian. The rise in $\delta^{34}\text{S}_{\text{in}}$ is correlated with the known record of increasing Ediacaran $^{87}\text{Sr}/^{86}\text{Sr}$, indicating a tectonic control on riverine sulfate delivery. The ~ 30 permil decline in $\delta^{34}\text{S}_{\text{SO}_4}$ observed in the Paleozoic is interpreted as representing in part the return of $\delta^{34}\text{S}_{\text{in}}$ toward bulk Earth values. Against this background of increasing Ediacaran $\delta^{34}\text{S}_{\text{in}}$, the Ara $\delta^{34}\text{S}$ enrichment is caused by an additional increase in f_{pyr} , which is most likely driven by enhanced primary production and increased sedimentation rates associated with the assembly of Gondwanaland. The data presented here constrain the changes in biogeochemical cycling that caused the Ara sulfur anomaly and serve as a contextual framework for understanding the E-C boundary, as well as biological and environmental change into the Paleozoic.

Micron-scale resolution of sulfur cycling in a microbial mat

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Microbial mats consist of finely laminated layers of diverse microbial communities. Mat organization is thought to result from strong spatial gradients in light intensity and redox in the uppermost few millimeters. Optical examination reveals microbial laminations on scales between 5mm and 5 μm throughout the thickness of the microbial mat. However, such fine laminations at depth have usually been regarded as a ‘relict architecture’ inherited from an older mat surface. To further our understanding of microbial processes within this laminated architecture, we have investigated sulfur cycling (as recorded by sulfide production) within a benthic microbial mat.

We present a high-resolution spatial profile of sulfide abundance and isotopic ($\delta^{34}\text{S}$) composition on the micron-scale through a microbial mat community analyzed using a Cameca NanoSIMS 50L ion microprobe. We find a fine-scale (0.1-2mm) banding of sulfide throughout the mats as visible to the naked eye. In addition, there are micron-scale ($\sim 4\mu\text{m}$) laminations observed using the NanoSIMS both in optical CCD and element scanning mode. We have mapped the sulfide $\delta^{34}\text{S}$ profile from the mat surface down to a depth of $\sim 1\text{cm}$ at $\sim 100\mu\text{m}$ resolution with a typical analytical error of $\pm 0.5\%$ (1σ). $\delta^{34}\text{S}$ varies over $\sim 25\%$ as a function of depth through the mat. An apparent oscillatory behavior in $\delta^{34}\text{S}$ exists over $\sim 4\text{mm}$, which approximates the spacing of the coarsest mat laminations. This result suggests that the deeper mat architecture reflects ongoing microbial activity rather than inherited architecture. At any given depth, there can be up to $\sim 5\text{-}10\%$ variability in $\delta^{34}\text{S}$ in immediately adjacent ($\sim 10\mu\text{m}$ apart) locations. High-resolution images (6-20 μm squares) of elemental abundance and isotopic composition indicate that the ubiquitous banding in sulfide abundance appears to control the $\delta^{34}\text{S}$ variability, with the offset between high- and low-sulfide regions up to $\sim 10\%$. Control experiments in standard solutions did not reveal any banding or the same scale of isotopic variability as observed in the microbial mat. We therefore believe that the banding and isotopic variability observed in the microbial mat are not an analytical artefact, but rather reflect very-fine-scale lamination in microbial activity preserved at depth within the mat, as is supported by microscopic observations. The environmental conditions that maintain such rigid laminations at depth ($\sim 1\text{ cm}$), far from the sharp redox gradients of the mat surface, remain poorly constrained; however, our results suggest that the full scope of sulfur cycling with microbial mats remains far from being completely understood or fully appreciated.

Structural incorporation of trivalent *f* elements into the trioctahedral clay mineral hectorite

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Clay minerals may play an important role in a high-level nuclear waste repository system. Clay-based materials have a high affinity for trivalent actinides, and several distinct molecular level mechanisms of actinide retention can operate: outer- and inner-sphere complexation, cation-exchange (interlayer), and structural incorporation.

Radionuclide immobilization by incorporation into the bulk structure of clay minerals may occur via coprecipitation. However, the size mismatch with the cations which typically occur in the octahedral sites of sheet silicates would result in large lattice strains [1]. Nevertheless, recent TRLFS data for Eu(III)/Cm(III) coprecipitated with hectorite at 90°C [2] suggest that such a substitution mechanism may operate [3,4].

Conventional EXAFS spectra collected on powders of Eu-containing hectorite suggested that Eu(III) was hexacoordinated with oxygens, as in a Mg structural site [5]. Neighbouring structural cations were not detected, maybe due to cancellation effects between EXAFS waves backscattered by (out-of-plane) Si and in-plane (Mg,Al) cations [6]. Polarized-EXAFS (P-EXAFS) experiments on self-supported films of these oriented clay minerals were thus carried out. Spectra were collected for varying europium contents to determine the influence of the degree of substitution on the local crystal structure.

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Potassium content in the Earth's core: A high-pressure and high temperature study of the Fe-K system

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The transition metal behavior of potassium at high pressure suggests that a significant amount of potassium could reside in the Earth's core. The radioactive isotope ⁴⁰K could indeed contribute to power the Earth's dynamo but a high concentration may prevent inner core formation. We report a diamond anvil cell study of the Fe-K system up to 42 GPa and 3000K. Using *in situ* X-ray diffraction carried out at the European Synchrotron Radiation Facility, we show that Fe and K can alloy in reducing conditions, provided the change in the chemical bonding character of K from alkaline- to transition-metal is complete (above 20-25 GPa). The incorporation of potassium causes iron lattice to expand with increasing potassium concentration. However, a precise determination of cell parameters of both Fe and K indicates that a maximum amount of 700±300 ppm in weight of K can be accommodated in the ε-Fe lattice. Such pure metal (K,Fe) experiments provide an upper limit to the potassium concentration in the Earth's core. Our estimate is lower than those proposed in previous studies and corresponds to a power limited to 4.3TW, may be more consistent with models of inner core growth and core-mantle boundary heat flow.

Hydrogeochemistry of alluvial groundwater in agricultural area: A case study in Gumushacikoy Aquifer, Turkey

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Ground and surface water quality can be affected by three different forms of pollution, which are chemical, biological and physical pollution. These polluting factors can influence natural environment and human health. Nitrates in soil and groundwater generally moves relatively slow and there is approximately 20 years lag time between the detection of the pollutant the pollution activity and in groundwater. In this study, groundwater pollution originated from agricultural activities and municipal wastewaters were investigated in Gumushacikoy urban area. The water analyses from 49 water wells in the plain, taken over a 2-year period, were used to determine the NO_3^- , NO_2^- and NH_4^+ contamination in the alluvial groundwater. The concentrations of nitrate (NO_3^-) in groundwater of Gumushacikoy Plain range from 0-15.61 mg/l, nitrite (NO_2^-) 0-0.007 mg/l and ammonium (NH_4^+) 0-0.5 mg/l. Most of the drinking water samples high in nitrite and ammonium concentrations and exceeding the limit of 0 mg/l (TSE 266, Turkish Drinking Water Standard). However other chemical parameters such as pH, EC, TH, Ca^{+2} , Mg^{+2} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{-2} and F^- were also measured. The pH and EC values of the well water samples are changing between 6.8 – 9.9. and 439-1276 respectively. Drinking water well of the some villages have low pH value according to the Turkish Drinking Water Standard. Total hardness of the groundwater samples are ranging between 2.5-57.75 according to the FH. These water samples range between “very soft” and “very hard”. Water type of the Gumushacikoy groundwater is Ca-HCO_3 . Carbonate hardness of the all drinking waters have bigger than %50. To the chemical analyse results, most of the well waters which are using for drinking purposes should not be used when considering to the NO_2^- , NH_4^+ , pH, total hardness. The present state of the quality of the Gumushacikoy alluvial groundwater necessitates taking some technical measurements in order to preserve and improve water quality.

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The concept of convergence in surface roughness and its relationship to rock and mineral surface reactivity

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In material science, the evolution of surface topography by processes such as abrasion has been traditionally quantified by roughness parameters. These parameters characterize quantitatively analyzed surfaces by a statistical treatment of {x, y, z} data. With this approach, we are able to quantify the evolution of surface deviations on a regular relief. However, complications arise because most natural rock surfaces show a multitude of wavelengths in terms of surface relief. To detect and quantify the alteration of rock surface topography, a statistical treatment of surface data must accommodate the occurrence of surface “building blocks” of different length. This is important because various surface building blocks typically show different reaction velocities during dissolution or precipitation.

Our approach makes use of so-called *convergent* surface roughness parameters, in which surface roughness parameters are calculated for differently-sized “footprints” from vertical scanning interferometry (VSI) data. We show several applications demonstrating the importance of convergent surface roughness parameters. In a study of oxidative weathering of organic matter (OM) in black shales, we can demonstrate that root mean square roughness (R_q) is tied to the distribution of OM components having a high reactivity for oxidative weathering. In a second study, convergent R_q data measured at iron oxide incrustations of oxidative-weathered uranium-bearing shale correlate linearly but inversely with the uranium (U) concentration of the incrustation. These surface data show a relationship between the occurrence of macropores ($d \sim 500$ nm) and the U content of the weathering product. As a third example, we demonstrate the application of surface roughness data to determine corrosion rates of volcanic glass surfaces. All examples underscore the importance of statistical surface parameters in the identification and characterization of the surface components that dominate reactivity.

Magnetite in bacteria: A FMR study

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Under controlled conditions, most of the known magnetotactic bacteria (MTB) precipitate intercellular magnetite crystals within membrane-bound organelles (magnetosomes). The magnetite crystals have an array of physical properties such as size and shape that fall within a narrow distribution. The magnetic properties of cultivated and wild magnetotactic bacteria have been studied in detail by classical rock magnetic methods. Recently ferromagnetic resonance (FMR) spectroscopy has been introduced as an additional tool to assess size and shape distribution in order to identify MTB. We used a pure culture of *Magnetospirillum gryphiswaldense* to analyse FMR effects of magnetite in MTB between 293 and 77K.

Under the TEM the MTB revealed chains of near-equidimensional magnetite crystals of about 50 nm in size which is characteristic for single-domain nanoparticles. For the FMR measurements the MTB were freeze-dried and fixed with paraffin in a glass tube.

At 293 K, the FMR measurement ($\nu = 9.5$ GHz) revealed an asymmetric spectrum with a line width of 187mT and a g-value of 1.885 (Figure 1). Considering the magnetite in the MTB as a "chain of spheres" the absorption spectrum is dominated by shape anisotropy. No angular dependence of the spectrum was found, which indicates a random distribution of the magnetite chains in the sample. At 77K a different FMR signal with a line width of 198 mT and $g = 2.24$ was observed. This temperature is below the Verwey transition ($T_v = 120$ K) where magnetite undergoes a crystallographic transition from cubic to monoclinic symmetry. Based on literature data, it can be postulated that the FMR spectrum at 77K is dominated by magnetocrystalline anisotropy. Considering the spectral development with temperature, the change from a shape-dominated to a magnetocrystalline-dominated anisotropy in the MTB at $T < 110$ K can be postulated (Figure 1).

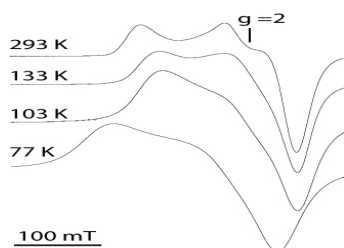


Figure 1: FMR spectra at 293, 133, 103, and 77K.

The spectral behavior of magnetite nanoparticles in chains at low temperature can be a diagnostic tool to detect magnetotactic bacteria in sediments and soils or magnetite arrays in geological environments indicative of bacterial origin.

Extreme oligotrophy in subsurface sediments of the South Pacific Gyre: Evidence from low oxygen fluxes

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To study subsurface microbial life at its energy limits, we investigated benthic microbial oxygen consumption as a key parameter for organic matter oxidation during an IODP site survey to the South Pacific Gyre in December 2006. The scientific goal of the expedition with the R/V Roger Revelle was to understand the nature of seafloor sedimentary life in the most ultra-oligotrophic oceanic region on Earth. Here, primary production, particle fluxes and sedimentation are extraordinarily low. We investigated benthic microbial respiration rates by measuring oxygen concentrations in sediments on different spatial scales *ex situ* (in piston, gravity and multi-cores), and *in situ* (using a benthic lander equipped with an incubation chamber, a microelectrode profiler, and an optode profiler). Along a transect from 24° to 46°S and 165° to 117° W, cores at 10 of 11 sites were oxygenated for their entire lengths (as much as 8m below seafloor), at concentrations $>150\mu\text{M O}_2$. This represents the deepest oxygen penetration ever measured in marine sediments. All profiles showed a similar pattern of a rapid decrease in oxygen concentrations from $\sim 220\mu\text{M}$ to $\sim 170\mu\text{M}$ within the first 50cm, which can be explained by oxidation of sedimented organic matter. In the deeper zones, only a very small gradient of $\sim 6\mu\text{M m}^{-1}$ was present, indicating extremely low oxygen fluxes and consequently low respiration rates.

We conclude, that the South Pacific Gyre represents the most oxidized and energy-limited marine benthic habitat on earth, with respiration rates at least 3 orders of magnitude lower than previously analyzed marine sediments.

The kinetics of biologically-mediated mineral oxide reduction and biomineralization using time-resolved X-ray diffraction

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The ways in which microorganisms catalyze or inhibit the breakdown and formation of minerals have broad implications for stable isotope geochemistry, acid mine drainage, climate change investigations, the search for life on other planets, and the evolution of life on this planet. We are investigating the kinetics of microbial-mineral interactions using X-ray diffraction (XRD), an old technique applied in a new way.

With the advent of the high-resolution imaging plate, we can take XRD scans in rapid succession (one every 2-10 minutes) and analyze changes in mineral phases as time progresses. This "time-resolved" XRD technique, combined with Rietveld analysis of the diffraction data, has allowed us to decipher discrete changes in unit cell parameters, phase abundances, and atomic displacements.

Total membrane (TM) fractions of the facultative anaerobe *Shewanella oneidensis* MR-1 can catalyze reduction of solid-phase metal cations (Ruebush *et al.*, 2006). In our experiments, these TM fractions were placed in a silica glass capillary with the manganese oxide birnessite, HEPES buffer (pH=7.0) and Na-formate, which serves as an electron donor. Using a Rigaku II D/Max X-ray microdiffractometer with a Mo-source, we succeeded in monitoring changes in mineralogy within the reaction cell. Our experiments revealed that the reduction of Mn began within minutes and continued until the birnessite had reacted completely. A secondary phase, rhodochrosite (MnCO₃), appeared upon the bioreduction of the birnessite.

We conducted the experiment at TM concentrations of 1.4 mg/ml and 3.5 mg/ml, Na-formate concentrations of 1M and 2M and total birnessite weights of .3 and .6 mg. The rate of reduction and re-mineralization was fastest with low TM and high formate concentration, and slowest with high TM and low formate concentration.

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Rhodium, gold and other highly siderophile elements in chondrites

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Osmium isotopic data and concentrations of the highly siderophile elements (HSE) Re, Os, Ir, Ru, Pt and Pd, recently obtained on chondrites by isotope dilution and Carius tube digestion in reverse aqua regia indicate systematic differences in the HSE composition of chondrite groups, notably in Re/Os and Pd/Ir. Unfortunately, these studies did not provide data for two other HSE, Rh and Au, because both elements are monoisotopic. Yet, Rh and Au may be critical elements for (1) a comprehensive understanding of the different HSE patterns of the chondrite groups and their origin; (2) distinguishing likely lunar impactor populations during the late heavy bombardment; and (3) for a complete characterization of the HSE pattern of the Earth's primitive mantle and its origin.

Here, we report abundances of Re, Ir, Ru, Pt, Pd, Rh and Au for a set of carbonaceous, ordinary, enstatite and R-chondrites. The new Rh and Au data, along with previous high-precision HSE concentration data on whole rocks of chondrites, require the presence of several distinct components in order to explain their CI-normalized patterns. (1) Carbonaceous chondrites show nearly flat HSE patterns from Re to Pt with CI-like or lower Re/Ir. Ordinary and enstatite chondrites show systematic fractionations from Re to Ir (decreasing) and from Ir to Pt (increasing) indicative for a complex high temperature history of ordinary and enstatite chondrites and the presence of at least two refractory components. (2) Most chondrites show a sometimes substantial drop in normalized abundance between Pt and Rh, suggesting the removal of a refractory metal phase from solar gas in a narrow temperature range (near 1400 K), and likely before condensation of the major fraction of Ni and Fe occurred (< 1350 K). (3) Chondrites are characterized by variable enrichment or depletion of Pd and Au, suggesting the variable presence of a component depleted in refractory siderophiles and enriched in moderately volatiles.

Search for an ^{60}Fe supernova-produced isotopic signal in marine sediments

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The recent observation of an ^{60}Fe peak in a deep-sea FeMn crust has been interpreted as due to the signature left by the ejecta of a supernova (SN) relatively close to the solar system 2.8 ± 0.4 Myr ago [1]. To confirm this interpretation with better time resolution and more direct flux estimate, we have performed Accelerator Mass Spectrometry (AMS) ^{60}Fe measurements along a dated marine sediment core.

FeMn crusts are authigenic objects. Marine sediments are composed of a larger variety of geochemical phases. Since the iron in the aluminosilicate phase is not equilibrated with the soluble ^{60}Fe in the ocean, its inclusion would lower the $^{60}\text{Fe}/\text{Fe}$ ratio compared to the authigenic fraction. Therefore, we used a chemical procedure to isolate this fraction [2]. The AMS measurements were carried out at the facility of Garching. In order to verify that our chemistry was dissolving the phase containing the ^{60}Fe seen in the crust, we tested it on samples from the same crust. We also observed an $^{60}\text{Fe}/\text{Fe}$ peak, consistent with that found by [1].

The ^{60}Fe signal in the FeMn crust was observed over a depth interval corresponding to 800,000 years [1]. However, we initially assumed that this was due to the inherent time resolution associated with the growth and sampling of the FeMn crust. Assuming a short deposition time e.g. 10,000 years [3], and considering the characteristics of the marine sediment core, we can calculate a $^{60}\text{Fe}/\text{Fe}$ ratio in the authigenic phase of the sediment of 5×10^{-14} .

We performed $^{60}\text{Fe}/\text{Fe}$ measurements along the sediment core from 1.7 to 3.2 Myr. The extension of the original time interval (2.4-3.2 Myr [1]) is from taking into account (i) that ^{10}Be dating has been repeated in the crust, (ii) $t_{1/2}(^{10}\text{Be})$ uncertainty.

We found no evidence for an $^{60}\text{Fe}/\text{Fe}$ peak in the sediment in the time interval 1.7-3.2 Myr, with upper limits at least an order of magnitude lower than the value expected under the above assumptions. We will discuss possible reasons for this result, including the possibility that the deposition time was indeed $\gg 10$ kyr.

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The groundwater beneath Hekla volcano, Iceland; A natural analogue for CO_2 sequestration

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The increased concentration of CO_2 in the atmosphere has made it necessary to develop methods to store CO_2 . One of the possibilities for CO_2 storage is by reacting it with basalt and thereby precipitating the CO_2 as calcite (CaCO_3). A pilot project is being performed in Iceland by Reykjavik Energy, University of Iceland, Columbia University and University of Toulouse.

The Hekla volcano is one of Europe's most active volcanoes (e.g. Flaathen and Gislason, 2007) and its magma chamber degasses even under quiet periods where the main emitted gases are CO_2 , HF and SO_2 . These are some of the same gases emitted from geothermal power plants and aluminum smelters in Iceland. This makes Hekla volcano a very good natural analogue to CO_2 sequestration in basalt.

The lava fields surrounding the volcano host a large ground water body. Water samples from its springs have been collected periodically for 20 years. Analysis and modelling of this water can tell us what may happen when CO_2 is being injected into basalt.

The gases emitted from the magma chamber make the ground water acidic. The acidity enhances the dissolution rate of the basalt releasing elements like Ca into the ground water. These reactions consume protons and the increase in concentration of elements in the ground water together with increase in pH leads to the precipitation of secondary minerals like calcite.

Modelling performed by the PHREEQC 2.11 computer code (Parkhurst and Appelo, 1999) shows that calcite goes from being undersaturated to almost saturated with increase in pH.

At the early state of dissolution of the basalt, at low pH, the concentration of toxic metals like Cr and Pb in the ground water might be high. The pH of the groundwaters in the vicinity of Mt. Hekla range from about 7 to 9. The concentration of toxic metals is very low in these waters (nmole/kg) which is also the case for Fe. Modelling shows that Fe-hydroxides are supersaturated in the groundwaters and the precipitation of this phase might scavenge the toxic metals.

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Investigation of weathering rinds on Earth and Mars by depth selective Mössbauer spectroscopy

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The two Mars Exploration Rovers, “Spirit” and “Opportunity”, each carry a miniaturised Mössbauer spectrometer (MIMOS II) [1]. MIMOS II operates in backscattering geometry and can obtain 14.4 keV gamma ray spectra and 6.4 keV X-ray spectra simultaneously. Comparing 14.4 keV and 6.4 keV spectra yields depth selective information about a sample: 14.4 keV gamma rays have a larger escape depth from a sample than 6.4 keV X-rays because of their higher energy. As a consequence, a 6.4 keV spectrum contains more information about the near-surface part of a sample than a 14.4 keV spectrum. This allows for the detection and characterization of coatings such as weathering rinds without abrading the surface of the sample.

At the landing site of the Spirit rover in Gusev crater, a dark coating was detected on the rock “Mazatzal” [2]. 14.4 keV spectra and 6.4 keV spectra obtained on the brushed surface of Mazatzal show significant differences in the relative intensity of “nanophase oxide”, a “poorly crystalline product of oxidative weathering that contains nanometer-sized particles of Fe³⁺-bearing material” [3].

To investigate the depth selectivity in Mössbauer spectra experimentally, measurements were done on samples composed of thin sections of one mineral or iron foil, respectively, on another mineral. The influence of coatings of varying thickness and composition on Mössbauer spectra can be studied in a simulation. A Monte Carlo simulation compiled for this work allows the modelling of a sample composed of two homogeneous layers, each containing up to ten different minerals. The thickness of a coating can be determined by comparing measured and the according simulated spectra. In the case of Mazatzal, modelling the coating with a thickness of 10 micrometers leads to best agreement between measured and simulated spectra. [4]

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Integrated air quality assessment – Pine needle $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ as proxy for atmospheric CO_2 and NO_x loads

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In a multidisciplinary approach atmospheric quality in the Greater Cologne Area (GCA) was studied using pine needles as pollutant bioreceptors. Here we discuss the potential of the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ isotopic composition of pine needle biomass to record the atmospheric loading with CO_2 and NO_x released from anthropogenic combustion processes. The gaseous pollutant load estimated by isotope proxies is compared and interpreted in concert with persistent organic pollutant as well as major and trace element concentration data.

The GCA comprises a variety of CO_2 and NO_x emission sources, including lignite fueled power plants, regions of high traffic density, domestic heating, intensive agriculture and large industrial complexes along the Rhine Valley. A substantial part of atmospheric CO_2 in large conurbations will derive from fossil fuel combustion. Two reaction modes for increased CO_2 in atmosphere are known. A fertilizing effect by which the addition of isotopically light CO_2 will lead to a decline in foliage $\delta^{13}\text{C}$ values. Conversely, high concentration of CO_2 will cause stress and trigger closure of stomata, resulting in heavier foliage isotopes. For 5 needle age classes taken separately in summer and winter a systematic trend to $\delta^{13}\text{C}$ values heavier by about 2.5 permil with age was noted, attributed to declining photosynthetic activity. Differences between locations were larger than within location. Although influenced by a variety of environmental conditions the significantly lighter $\delta^{13}\text{C}$ of pine needles in urban Cologne reflects traffic emissions. The area affected by lignite combustion revealed no deviation in foliage $\delta^{13}\text{C}$ due to more intensive air mixing in these regions.

The $\delta^{15}\text{N}$ values of vegetation have been shown react to NO_x in surrounding air via direct stomatal uptake or via precipitation and root uptake. Hereby pollution stress induces heavier $\delta^{15}\text{N}$ values. Most often foliage and soil $\delta^{15}\text{N}$ are decoupled emphasizing the importance of atmospheric NO_x uptake and remineralization for foliage N-isotopes.

Investigation of 5 needle cohorts shows a systematic trends towards slightly lighter $\delta^{15}\text{N}$ values with age. Intra-site variability was low but inter-site variation high, allowing for excellent spatial discrimination. The $\delta^{15}\text{N}$ of pine needles showed a trend to heavier values in farming and forested areas but lighter values in urbanized regions and in areas affected by lignite mining. A trend inversion occurred in inner city areas, where changes from high to low $\delta^{15}\text{N}$ were noted. Heavier N-isotopes of foliage caused by NO_x -stress are in compliance with previous observation but seem to be restricted to areas most affected by traffic emissions.

The weathering engine conveyor belt and corestone size distributions

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In weathering profiles developed at Gettysburg (Pennsylvania, U.S.A.), unweathered diabase bedrock fractures and chemically alters by spheroidal weathering to produce a population of corestones surrounded by rindlets overlain by saprolite. It appears that once corestones reach a limiting size they no longer form new rindlets but weather strictly by a diffusion-limited infiltration mechanism.

We model the gross features of the chemistry and mechanics of rindlet formation and the production of weatherable surface area for a steady erosion rate W . The model yields a steady state profile of corestone volume fraction, f_C , decreasing upwards to the erosional surface from a value $f_C \approx 1$ at a depth, H , where chemical weathering is negligible. Populations of corestones in eroding or eroded material and initial block sizes were determined for the Pennsylvania diabase. The model, analogous to a conveyor belt, was fit to these data using a partial set of independently-estimated parameters in order to constrain the remaining parameters and to investigate the model. The model can be used to calculate the average size of corestones produced by the conveyor belt.

In addition, we have chemical and mineralogical data for 4 meters of saprolite developed on the same diabase versus depth that document the weathering reactions. Two depth intervals are observed where plagioclase and augite are weathering. An upper interface occurs at approximately 125 cm and appears to be coincident with maximum concentrations in organic acids. An additional reaction front is located at approximately 350 cm. We are seeking to develop a model that incorporates both chemical weathering reactions and evolution of corestone and mineral grain sizes as a function of depth.

Solubility of pyromorphite-mimetite solid solutions at 5-65°C: Variability of thermodynamic stability of minerals from pyromorphite – mimetite series at 5 - 65°C

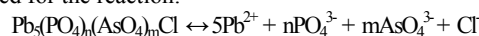
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The precipitation of pyromorphite and mimetite are effective methods of immobilizing toxic ions in contaminated soils and wastes (Maneck *et al.* 2002; Comba *et al.*, 1988). Though the solid solution series of these minerals is confirmed to be continuous, our knowledge about thermodynamic properties of pyromorphite and mimetite and their solid solutions is sparse (Nriagu, 1973; Ingbenebor *et al.*, 1989; Bajda *et al.* 2006).

Solubility of seven synthetic phases from pyromorphite - mimetite solid solution series was measured for three months in dissolution experiments at 5, 25, 45, and 65°C at pH=2 in 0.05 M KNO₃ background electrolyte. Plateau on [Pb] evolution patterns was used to determine equilibrium. This was confirmed by precipitation experiments.

There is a linear increase in solubility constant $\log K_{SP}$ calculated for the reaction:



with increasing As content in the series, from -79.60±0.02 for Pb₅(PO₄)₃Cl, through -78.54±0.2 for Pb₅(PO₄)_{1.5}(AsO₄)_{1.5}Cl, to -76.32±0.25 for Pb₅(AsO₄)₃Cl at 25°C. For all phases the solubility product decreased linearly with the inverse temperature indicating a constant enthalpy of dissolution reaction in the experimental range.

For pyromorphite Pb₅(PO₄)₃Cl: $\Delta H_f^\circ = -4096 \pm 10$ kJ/mol, $S_f^\circ = 665 \pm 33$ J/mol, $\Delta G_f^\circ = -3765 \pm 10$ kJ/mol.

For Pb₅(PO₄)_{1.5}(AsO₄)_{1.5}Cl: $\Delta H_f^\circ = -3542 \pm 14$ kJ/mol, $S_f^\circ = 635 \pm 46$ J/mol, $\Delta G_f^\circ = -3203 \pm 14$ kJ/mol.

For mimetite Pb₅(AsO₄)₃Cl: $\Delta H_f^\circ = -2985 \pm 17$ kJ/mol, $S_f^\circ = 599 \pm 55$ J/mol, $\Delta G_f^\circ = -2636 \pm 17$ kJ/mol. A linear increase of ΔH_f° and ΔG_f° and a linear decrease of S_f° with increasing As content in the series are apparent.

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The Ordovician Galiñeiro peralkaline gneiss complex, Vigo, NW Spain

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The Variscan mountain chain in Brittany (France), NW Spain, Portugal and SW Spain contains numerous orthogneiss complexes of early Paleozoic age, predominantly cropping out in the central zone of the orogen. Most have calcalkaline, alkaline and some peralkaline compositions. The first two are cut by numerous basic dikes.

The Galiñeiro peralkaline complex, situated mainly South of the city of Vigo near the Atlantic coast, is the largest and best investigated of these complexes. Fieldwork and petrographic studies done by the first author in the fifties and sixties of last century were followed in the eighties and nineties by detailed mineralogical and geochemical work by the third and second authors.

The results of both studies are highly complementary and give evidence of rock and mineral behaviour both at the intrusive stage and under Hercynian lowP, intermediateT metamorphic conditions leading to strong recrystallization, including total unmixing of the supposed original hypersolvus feldspar.

The rocks of the complex are enriched in REE and HFSE, present in a wide variety of accessories: bastnäsite, REE silicates (e.g., allanite, thalenite-yttrialiet), REE niobotantalates (aeschnyrite, fergusonite-formannite, samarskite, pyrochlore-betafite), REE phosphates (monazite, xenotime), Th-rich minerals (thorite, P-rich thorite), and zircon.

Magmatic fractionation, most likely from a mantle-derived volatile-rich alkaline basalt parent, led to peralkaline silicic differentiates with residual fluids extremely enriched in fluorine and other ligands, which complexed the REE and HFSE. Decrease in fluorine activity with falling temperature and the crystallization of F-bearing major minerals caused the breakdown of complexes, releasing the rare earths and the remainder of the high-field-strength elements, and formation of HFSE- and REE-rich minerals.

The elevated fluorine, CO₂ and sulfide contents of the Galiñeiro system, together with the energy inputs of the different phases of Hercynian metamorphism, caused episodic remobilisation, reflected by the zircon U—Pb concordant ages at 370 and 310 Ma, and the exotic geochemical features (Zr/Hf > 100, elevated levels of Be, Th, and HREE) of some samples.

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The functional species of a mineral surface and their interaction with the adjacent water molecules – Determined by nonlinear optics and quantum chemistry

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The functional species of the mineral surfaces, which control the mineral/water interaction, are not definitely known for most crystal faces because it is difficult to obtain chemical in situ information with interface selectivity. Here we apply interface selective vibrational sum frequency spectroscopy to the sapphire (001) surface. Additionally we carry out density functional theory and ab initio calculations on aluminium-oxide clusters as models for the sapphire (001) surface. The results of experiment and theory are well in agreement. This work is part of an ongoing fundamental study of the sorption mechanism of actinides on single crystal faces by various experimental and theoretical techniques. Sapphire serves as a simple model for natural clay minerals.

From the ideal termination of the bulk crystal structure, the (001) surface is expected to exhibit a single type of aluminol species with the OH group in a bridge position. We distinguish four OH species which are all doubly coordinated but exhibit different tilt angles of their OH bonds. Depending on the tilt, different geometries arise for hydrogen bonding with water molecules. At high pH the interaction of the mineral surface with the neighboring water molecules is dominated by electrostatic forces. The net dipole moment of these water molecules points into the direction of the mineral surface which is in agreement with the expected negative surface charge. In the pH range between 1.3 and 6 the interaction of the water molecules with the mineral surface is dominated by hydrogen bonds. Two populations of water molecules exist near the interface which are characterized by specific hydrogen bonding to the different aluminol species. Due to these bonds the net dipole moment of one water population points to the mineral surface, the net dipole of the other population points into the opposite direction. Since the relative concentrations of the different aluminol species depend on the pH, the relative concentrations of the two water populations changes also. In summary, a picture at the molecular level with surprising richness of details is obtained.

(U-Th)/He apatite constraints on the erosional history of the southwestern Colorado Plateau and implications for Early Tertiary uplift and carving of a “proto-Grand Canyon”

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Resolving the timing and relationships between regional unroofing, canyon incision, and topographic uplift in continental plateaus is a challenging problem. The regional unroofing history of the Colorado Plateau, and its relationship to Grand Canyon incision (up to 1.5 km) and plateau uplift (~1.9 km) since the Late Cretaceous, is controversial. We used (U-Th)/He apatite thermochronometry (36 samples, 230 single-grain analyses) across the southwestern quadrant of the Colorado Plateau to address these issues. Our data document overall southwest to northeast unroofing from plateau margin to plateau interior, during denudation phases in the Late Cretaceous/Early Tertiary (80 to 55 Ma), mid Tertiary (28 to 16 Ma), and Late Tertiary (<6 Ma). Distributions of apatite dates modeled using the radiation damage trapping model [1,2] suggest that eastern Grand Canyon samples from the basement and the Kaibab surface nearby had similar Early to mid-Tertiary thermal histories, despite their ~1500 m of stratigraphic separation. If these models are correct, they indicate that a significant (≥ 1000 m deep) paleo-Grand Canyon was carved in post-Paleozoic sediments in this region during Early Tertiary time. Evidence for kilometer-scale topographic relief would require substantial uplift during Sevier/Laramide time, preceding regional unroofing of this portion of the plateau interior. Although the data do not preclude additional post-Laramide uplift, the subsequent regional unroofing phases could be explained by drainage reorganization associated with rift-related lowering of adjacent regions without additional elevation gain of the plateau.

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A Comparison of the elemental composition of Wild 2 grains with other extraterrestrial materials

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NASA's Stardust spacecraft passed through the dust coma of Comet 81P/Wild 2 at a speed of ~6 km/s in January 2004, collecting dust particles in low-density silica aerogel and as impact residue in craters in Al-foil. These samples, which were delivered to Earth on January 15, 2006, provided the first opportunity to analyze material from the Kuiper Belt, the presumed source of short-period comets like Wild 2. The elemental compositions of twenty-three particles captured in aerogel and the residue in seven craters in Al-foil were determined during the Stardust Preliminary Examination (Flynn *et al.*, 2006). The results were generally consistent with the more limited elemental composition data obtained on grains from Comet 1P/Halley, an Oort cloud comet, which were analyzed by impact-ionization mass spectrometers on the Giotto and VEGA spacecraft which flew through the Halley coma in 1986.

To first-order, the mean elemental composition of the Wild 2 particles agrees with the composition of the CI carbonaceous meteorites, which are believed to represent the initial composition of the Solar System, for the refractory elements. However the Fe/Si ratio is somewhat lower than CI in the Wild 2 particles. In addition, S is depleted relative to the CI abundance and several moderately-volatile minor elements (Cu, Zn, Ga, and Ge) are enriched in the Wild 2 samples over the CI meteorite abundances.

Both the depletion of Fe and the enrichment of moderately-volatile elements were previously reported in the fine-grained, anhydrous IDPs, some of which have inferred atmospheric entry speeds suggesting a cometary origin (Brownlee *et al.*, 1993). The CI meteorite element abundances are taken to represent the Solar Nebula composition for non-volatile elements because of the good agreement between CI abundances and the composition of the Solar photosphere, measured by spectroscopy. These preliminary results on the Wild 2 material suggest that the outer region of the Solar Nebula, where comets such as Wild 2 are believed to have formed, may have contained higher concentrations of some moderately-volatile elements and lower Fe than the inner region of the Solar Nebula, where the meteorites formed. Alternatively, since the abundances of Cu, Zn, and Ga are not well-determined in the Solar photosphere, it is possible that abundances of these elements in the Wild 2 particles and the anhydrous IDPs may better reflect the composition of the Solar Nebula for these moderately-volatile elements than does the composition of the CI meteorites.

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Modeling silicate-rich fluids at high pressures

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Comprehension of rock-forming processes at depths corresponding to the lower crust and active subduction zones requires an understanding of silicate-rich fluids coexisting with rock-forming minerals. However, existing models for aqueous silicate solutions are difficult to extrapolate to pressures higher than 0.5 – 1.0 GPa. An alternative approach is to treat H₂O in terms of a statistical thermodynamic model involving a dynamic equilibrium between "gas-like" disordered and "liquid-like" clustered molecules (Gerya and Perchuk, 1997; Gerya *et al.*, 2004), where X(liq) is the mole fraction of the latter. Gerya *et al.* (2005) successfully tested this approach for SiO₂-H₂O solutions to 1300°C and 2 GPa. We extend this model to include the ionization of water, combining available and also new experimental solubility data for quartz (SiO₂), corundum (Al₂O₃), wollastonite (CaSiO₃), grossular (Ca₃Al₂Si₃O₁₂), zoisite (Ca₂Al₃Si₃O₁₂(OH)), sanidine (K_{0.9}Na_{0.1}AlSi₃O₈) and albite (NaAlSi₃O₈) in pure H₂O, as well as quartz and corundum solubilities in KOH solutions, to develop a simple thermodynamic description for aqueous fluids in the model system KNCASH. ΔG_r of dissolution reactions is thus expressed in terms of the standard-state molar thermodynamic parameters ΔH_r° , ΔS_r° , $\Delta Cp(T)_r$, $\Delta V(T,P)_r$, the molality of the dissolved species, pH and X(liq). The model successfully returns the available experimental data. The formalism requires data on speciation to define the influence of X(liq) and pH on the reaction and to determine the number of species and reactions involved. However, a simplified "component" approach for oxides can be developed to approximately model KNCASH fluids from 0.2 to 3 GPa. The incorporation of pH into the model reduces the need for "mixing terms" to describe the interaction of dissolved oxides. Calculations suggest the formation of alumina-silica, alkali-silica, alkali-alumina as well as silica-alumina-alkali species. This information can also be directly derived from a comparison of the different experimentally investigated fluid-solid systems. There is no indication at present for the formation of multi-oxide complexes with Ca.

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Cosmogenic ³He exposure dating of the Quaternary lavas at Fogo, Cape Verdes: Dating flank collapse and magmatic reorganisation

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Construction and destruction of young ocean island volcanoes is often episodic and governed by periods of intense volcanism and flank collapse. Conventional dating methods are often insufficient to constrain late Quaternary events; rocks may be too young to be dated precisely by ⁴⁰Ar/³⁹Ar, or lack datable material (e.g. charcoal) for ¹⁴C. Cosmogenic ³He exposure dating of basaltic lavas is a powerful alternative, with potential to date flows beyond a few kyr. We present results from a study to date Quaternary lavas of Fogo, Cape Verdes. The growth of Fogo occurred in two main stages, separated by a large flank collapse removing the summit and eastern flank of the pre-collapse Monte Amarelo volcano. The collapse produced a 9 km wide escarpment with a headwall cliff that is still 1 km high despite the infilling with over 1.5 km of post-collapse lava flows from the Cha das Caldeiras volcano. Dyke swarms in the Monte Amarelo volcano indicate that the collapse was preceded by a structural reconfiguration of an initially radial dyke swarm to a single, dominantly north-south swarm across the summit region. This coincided with an eastward shift in magmatic activity. The recent history of the Cha das Caldeiras volcano has seen similar structural reconfiguration of dyke swarms and eastward shift of volcanism resulting in the extinction of post-collapse volcanic rift zones in the west of the island. Dating these events is vital for understanding the timing of (future) volcano flank collapses of Fogo.

Lava flows erupted immediately prior to, and after the collapse bracket its age and exposure ages from two pre-collapse ankaramite flows yield 24 and 110 ka, while post-collapse flows yield 14 to 9 ka. We infer two possible scenarios; (i) the collapse occurred between 14 and 24 ka or, (ii) the young exposure age of the pre-collapse flow is an artefact of ash cover/erosion and collapse occurred closer to 110 ka. This has profound implications for the interpretation of future flank collapses on Fogo. The post-collapse flows are among the youngest flows on the western side and the early Holocene ages imply that the magmatic reconfiguration and possible onset of renewed instability of the eastern flank has been developing for several thousand years. If the collapse occurred between 14 and 24 ka, flank instability may be in its early stages. If the collapse occurred around 110 ka, the duration of the pre-Monte Amarelo collapse reorganization may be comparable to the duration of the present one, with the prospect of a near-future collapse likely.

Trace metal dynamics and transport in a polar glacier-dominated watershed: Taylor Valley, Antarctica

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Anthropogenically introduced trace metals travel to even the most remote locations on earth including Greenland and Antarctica. Little is known about metal dynamics in the largest ice-free area in Antarctica, the McMurdo Dry Valleys, which includes Taylor Valley (~78°S). Previous work has examined metal concentrations in Taylor Valley glacier melt streams and lakes (Green *et al.*, 1989; 1986). In this work, concentrations of metals (V, Pb, Cd, Cu) in Canada Glacier snow is compared to stream and lake concentrations to determine melt evolution and to ultimately make predictions about stream chemistries.

Samples were collected using ultraclean techniques to minimize contamination. The sequence of median trace metal molar abundance in Canada Glacier snow is Cu>V>Pb>Cd. Canada Glacier's melt streams have different relative abundances than the snow. The western melt stream, Andersen Creek is V>Cu>Cd>Pb. Whereas the eastern melt stream, Canada Stream, is Cu>V>Cd>Pb. Median Na:Cl ratios increase from snow values (0.4) in both Andersen Creek and Canada Stream (0.9), suggesting in-stream chemical weathering and salt dissolution. The western and eastern lakes fed by these streams, Lake Hoare and Lake Fryxell have similar Na⁺:Cl⁻ surface water values as the streams. In general V, Cu, Cd, and Pb to Cl⁻ ratios are all highest in Canada Glacier snow and lowest in its streams. The exception is Cu:Cl⁻, which is highest in lake surface water followed by snow and streams. Total Hg:Cl⁻ ratios in the Lake Fryxell Basin indicate substantial removal of Hg relative to Cl⁻ as the waters evolve from snow to lake with the largest losses occurring from stream to lake (Lyons *et al.*, 1999). There is no net gain of trace metals relative to Cl⁻ through weathering as with Na⁺. Their concentrations relate more to other processes such as adsorption, biotic uptake and/or removal by suspended material, which are connected to discharge, pH, and biomass abundance.

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Quaternary records of ocean pH

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Atmospheric CO₂ (pCO₂) is an important greenhouse gas that regulates the Earth's climate on geological and shorter timescales. Proxy data for the ocean carbonate system in the past have a crucial role to play in the understanding how CO₂ is partitioned between the ocean and the atmosphere on these timescales. Of particular importance in this regard are the suite of proxies based on the isotopic and trace element composition of foraminifera, and in particular, the isotopic composition of boron ($\delta^{11}\text{B}$) which a number of studies have shown faithfully records the pH of seawater in which the foraminifera grew.

There are a number of factors complicating the application of the boron isotope pH proxy, some of which arise from the analytical difficulties involving the precise and accurate measurement of its isotopic composition. We have recently developed an approach, using multicollector inductively coupled plasma mass spectrometry, that overcomes these analytical problems. This technique is both rapid and precise (better than 0.3 ‰) allowing the routine determination of $\delta^{11}\text{B}$ in a small number of foraminifera. We present here the first application of this technique.

In contrast to previous work we find that the measured isotopic composition by MC-ICPMS for a variety of Holocene species (ranging in $\delta^{11}\text{B}$ from 16 to 21 ‰) from a range of depth habitats and physiology, is very close to that of the dissolved B(OH)₄⁻ species predicted using an isotopic equilibrium constant of 1.0272 [1] and pre-industrial carbonate system parameters. This result greatly simplifies the use of the proxy. In this contribution we determine Quaternary and Late Neogene changes in pH on various timescales in several localities in the equatorial oceans (Caribbean, Eastern Atlantic, Western & Eastern Pacific). Using these data to gain a global perspective, we can distinguish local short term changes in pH from changes relating to the global reorganization of the carbonate system that accompanied glacial-interglacial climate change, and use our pH reconstructions to estimate the magnitude of pCO₂ changes beyond the reach of the ice-cores.

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³He from extraterrestrial dust as a constant flux proxy: Estimation of the present-day flux

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Extraterrestrial ³He is delivered to the earth surface by interplanetary dust particles (IDPs) characterized by a very high ³He/⁴He ratio (2.4×10^{-4}), several orders of magnitude higher than ratios measured in terrigenous matter (e.g. review by Farley, 2001, and Schlosser and Winckler, 2002).

Several recent studies in marine sediments (Marcantonio *et al.* 2001, Higgins 2001) and polar ice (Brook *et al.* 2000, Winckler and Fischer 2006) have opened up the application of extraterrestrial ³He as a constant flux proxy, at least over the last 400 ka, with a mean flux around $8 \pm 3 \times 10^{-13}$ ccSTP/cm²/ka. In order to measure the present ³He_{ET} flux, we started in 2001 to collect dust in the Paris region every two months, corresponding to an area-time product of 0.03 m².a.

As expected from such small area-time products, the data are scattered due to the small number of IDPs sampled, preventing the observation of any seasonal variability: the observed total ³He flux range from 1 to 200×10^{-13} ccSTP/cm²/ka, with a mean value of $(32 \pm 9) \times 10^{-13}$ ccSTP/cm²/ka. However, ³He/⁴He ratios are often below 10^{-7} and the terrestrial ³He component has to be estimated. Our measurements can be considered as binary mixings between an IDP and a terrigenous end-member with a ³He/⁴He ratio of 1×10^{-8} , leading to an estimate of the present ³He_{ET} flux of $(30 \pm 9) \times 10^{-13}$ ccSTP/cm²/ka.

This flux is significantly higher than the mean accepted value of $8 \pm 3 \times 10^{-13}$ ccSTP/cm²/ka, which is all the more surprising that we would expect statistical underestimation due to the small area-time products sampled, especially compared to marine sediments where values up to 0.2 are frequent (Farley *et al.*, 1997). Different explanations can be considered: (1) There may be temporal variations which are smoothed in sediments. For instance, Brook *et al.* measured values of 22 and 25×10^{-13} ccSTP/cm²/ka around 93 ka in Vostok ice. (2) Lateral winds may remobilize dust with IDPs in addition to the vertical flux.

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Chemical and isotopic constraints on water/rock interactions at the Lost City hydrothermal field, Mid-Atlantic Ridge

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Low temperature vent fluids issuing from the ultramafic-hosted hydrothermal system at Lost City, 30°N Mid-Atlantic Ridge, are enriched in dissolved volatiles (H₂, CH₄) while attaining elevated pH values, indicative of the serpentinization processes that govern water/rock interactions deep in the oceanic crust. Most importantly, serpentinization described mainly by the exothermic hydrolysis of Fe-bearing olivine has been directly linked to the heat source that drives seafloor hydrothermal alteration at Lost City. The extent of exothermic heat generation, however, has been shown to be strongly dependent on the availability of fresh peridotite, with theoretical calculations indicating that low fluid/rock mass ratios (<1) are prerequisites for exothermic reactions to be the primary source of heat in this system [1].

Based on the Sr and ⁸⁷Sr/⁸⁶Sr composition of vent fluids sampled from Lost City [2], however, estimations of the integrated w/r ratios range between 6 and 8. Furthermore, constraints on the fluid/rock mass ratios together with reported ^δ¹⁸O isotopic vent fluid compositions (0.7‰) permit seafloor reaction temperatures in excess of 250°C to be approximated, following the temperature-dependent oxygen isotope fractionation between serpentine and water. These estimations are in general agreement with previous theoretical studies [1], further supporting, however, extensive conductive heat loss occurring within the upflow zone of the Lost City hydrothermal system. Evidence of such extended conductive cooling stage include the relatively elevated precipitation temperatures (130-220°C) predicted by the negative ^δ¹⁸O composition values (<-14.2‰) reported for carbonate veins in basement peridotite. In addition, endmember dissolved boron concentrations of the Lost City vent fluids (~30 μmol/kg) [3] are significantly lower than those measured in other MAR hydrothermal systems, while with ^δ¹¹B isotopic composition maintaining values (~30‰) [3] reflective of elevated temperature hydrothermal alteration conditions, an substantial boron uptake into secondary phases along the discharge zone can be suggested; a process consistent with the proposed extensive conductive cooling that appears to greatly affect the chemical evolution of the Lost City hydrothermal vent fluids.

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Geochemical anomalies in stream sediments of the upper Sava River drainage basin (Croatia, Slovenia), determined by statistical methods

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Introduction

Sava River is a transboundary river of supraregional interest, draining 95,719 km² in Slovenia, Croatia, Bosnia and Herzegovina and Serbia. It is a typical Alpine river, flowing from Julian Alps. It becomes a typically lowland river when entering Croatia. The upper flow of Sava River can be compared with Soča/Isonzo River, which flows from the other side of Julian Alps toward Adriatic Sea.

The aim of the work was to extend the mineralogical and geochemical dataset of stream sediments from Upper Sava River and to study the possible influence of sub-basins of Savinja, Krka and Kupa rivers on main course of Sava River.

Methods

Mineral composition was determined by X-ray diffraction and chemical composition by inductively coupled plasma mass spectroscopy (ICP-MS). Two different procedures to identify anomalous geochemical data were used: the box plot method and the median absolute deviation (MAD).

Results and discussion

Results obtained by the box plot method showed that anomalous concentrations (extreme or outlier) of Zn, Pb, In, Cu, Co, Se, Zr, Cd, As, K, Na, Tl, Ba, B, Mn, Fe are present in sediments of the Celje region, of Cr, Ni, S, In, Cu, Mo, Pb in Moste Dam (pollution traced down to camping Šobec), and of Hg in Litija-Zagorje mining region. The MAD method is more sensitive. It depicts the same polluted areas, but with more anomalous values, which are above threshold values for toxicity. Both statistical methods (box plot and MAD) show two anomalous values for Hg in Sava River near Kranj and Zagorje. The concentrations are much higher than those causing significant toxic effects (>2 ppm). The two locations of Sava River in Croatia show very clean environment with respect to trace elements, although Sava River passed big cities of Zagreb and Sisak. The results clearly indicate self-purification mechanisms of Sava River.

Recommendations and perspectives

Similar future sediment study is recommended on middle and lower Sava drainage basin of interest for Croatia, Bosnia and Herzegovina and Serbia to detect possible pollution centers. In the case of significant pollution, remediation of sediments and watershed management should be applied.

Isotopic and geochemical evidence of gas producing microbial ecosystems in coal seams and gobs in the SW Upper Silesian basin, Czechia

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Gas habitat

Gas samples were collected from coal seams of Namurian A-C age, gobs and overburden reservoirs in the Late Carboniferous Upper Silesian basin (USB), NE Czech Republic. The $\delta^{13}\text{C}$ values of methane and $\text{C}_1/(\text{C}_1+\text{C}_2)$ ratios suggest occurrence two genetic types of gases. (Fig. 1).

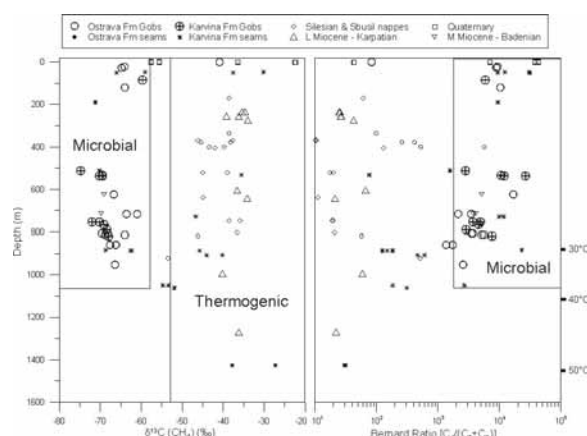


Figure 1: Isotopic and molecular composition of gases versus depth in different geological setting.

Discussion of the results

Thermogenic ^{13}C enriched and wet gas is extracted from the unmined seams in the Ostrava Fm. Dry and isotopically light gas is encountered in the gobs as reported also from Polish mines (Kotarba 2001).

Conclusions

Presence of microbial gas in the USB evidences activity of deep biosphere down to depth of 1000 m. Supply of oxygenated compounds and H_2 is the limiting factor of microbial activity (Horsfield *et al.* 2006). The temperature conditions of are favorable for methanogenesis at dept range up to 2 km (70°C).

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Hydrothermal stability of adenine under controlled fugacities of N₂, CO₂ and H₂

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Demonstrating that organic compounds are stable at high temperatures is important in the context of Archean hydrothermal systems as potential sites for the synthesis of the first organic molecules on Earth. Among such molecules, amino acids have been the subject of numerous studies (e.g. Miller and Bada, 1988; Shock, 1990; Andersson and Holm, 2000). In contrast, nucleic acid bases have received much less attention. Consequently, the present experimental study was undertaken to investigate the stability of adenine at 300°C. The experiments were carried out in sealed autoclaves under fugacities of gaseous CO₂, N₂ and H₂ representative of those encountered in marine hydrothermal systems. The fluid phase was generated from the decomposition of oxalic acid, sodium nitrite and ammonium chloride, and the oxidation of metallic iron. The results of the experiments seem to indicate that the concentration of adenine stops decreasing after ~ 96 hours (Figure 1). This suggests that an equilibrium state may have been established between adenine and the inorganic constituents of the fluid phase, which is corroborated by independent thermodynamic calculations.

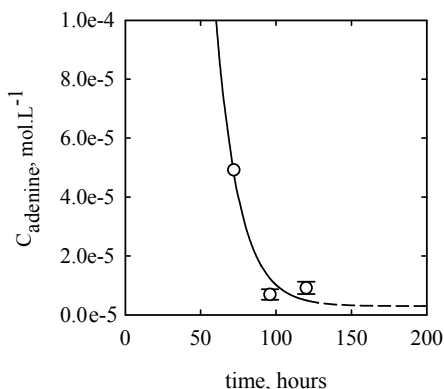


Figure 1: Evolution of the concentration of adenine as a function of time. The dashed extension represents an extrapolation beyond the duration of the experiments.

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The importance of constant flux proxies in paleoceanography

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For all paleoceanographic reconstructions from marine archives a precise chronology is the most essential prerequisite for reliable estimates of processes in the past and for compatibility between different records. All paleoceanographic studies, in particular those aiming at the reconstruction of fluxes from pelagic sediments (for example those on paleoproductivity or dust fluxes) face two main additional problems which complicate a reliable application. For some components of interest (such as organic carbon or biogenic opal) only a small and even variable fraction may be preserved between signal formation in surface waters and deposition in the sediments. The second problem which can affect all paleoceanographic reconstructions from marine sediments is sediment redistribution by currents or within nepheloid bottom layers. These processes can alter the true signatures to variable extents thereby completely masking the original signatures. This is of course particularly important in dynamic bottom current regimes but sediment redistribution can also be active at any other location.

In order to overcome and, in the optimal case, quantify and correct for these effects, a number of so-called constant flux proxies have been developed and applied. The most frequently used of those is the U-series nuclide ²³⁰Th, which is produced at a constant rate in the water column of the Ocean from homogeneously distributed uranium, and which is only advected with water masses to a very limited extent due to its high particle reactivity. Other examples are ³He derived from interplanetary dust particles (IDPs), which are deposited on the surface of the earth at a nearly constant rate or, less frequently used, cosmogenic ¹⁰Be.

I will give an overview of these constant flux proxies and discuss recent new findings on their strengths and weaknesses. As in most cases in paleoceanographic and geochemical research, none of these proxies is perfect but in view of the possibly huge misinterpretations occurring without their use, their application is absolutely crucial for any reliable paleoceanographic reconstruction. This is because effects of sediment redistribution cannot be readily identified from sedimentary parameters, they may occur at unexpected locations, and places with potentially focussed sediments are preferentially chosen as coring sites due to the expectable high time-resolution of the records.

Geochemistry and petrology of granulite-facies rocks from Rogaland, SW Norway

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High-grade metamorphic ortho- and paragneisses are exposed in the proximity of the 0.9 Ga Proterozoic Rogaland anorthosite massif, SW-Norway. The study area is located 5-20 km northeast of the intrusive contact with the anorthosite. In this area, migmatitic opx-bearing granitic gneisses are the main rock type present, transected by metabasites as dykes. Minor migmatitic garnet-sillimanite-cordierite gneisses, quartzites, calc-silicate rocks, marbles, and rare sapphirine granulites occur as folded layers or discontinuous lenses in between large Opx-gneiss bodies. They aim of the present study was to elucidate the composition of the protoliths of the different rock units, to reconstruct their tectono-metamorphic evolution, and to investigate the influence of a possible contact-thermal overprint related to the emplacement of the Rogaland anorthosite massif.

Regarding their geochemical characteristics, the Opx-gneisses can be classified as granites, granodiorites and diorites. They are peraluminous in composition and mainly show I-type to S-type, post-collisional granite signatures. Protoliths of the metabasites are tholeiitic mid ocean ridge basalts, whereas those of the paragneisses mainly comprise arkosen and greywackes.

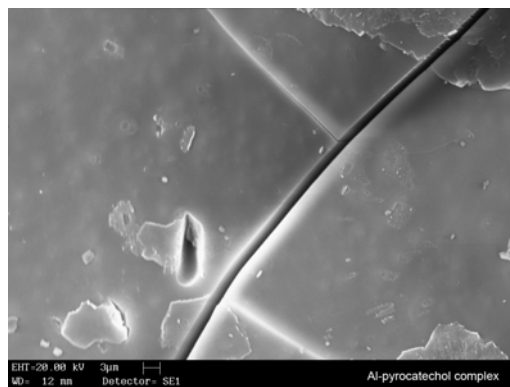
All rock units experienced high-grade regional metamorphism with associated ductile deformation and partial melting. The peak-metamorphic assemblage of the Opx-gneisses is garnet-orthopyroxene-plagioclase-quartz, whereas that of the metabasites is orthopyroxene-clinopyroxene-plagioclase-quartz. Retrograde biotite and amphibole define a strong foliation. For the thermobarometric calculations Opx-gneiss and metabasite samples from 5 km up to 20 km distance to the anorthosite contact were chosen. For all samples similar granulite facies peak-metamorphic conditions of 900 ± 100 °C at 6 ± 1 kbar are calculated, providing evidence against a contact-thermal effect related to the emplacement of the Rogaland anorthosite. Following this, contact-metamorphism induced by the anorthosite emplacement, as evidenced by pigeonite-in and osumilite-in isograds, is restricted to a distance of < 5 km to the contact.

Characterization of aluminum-pyrocatechol complexation in aqueous systems using ultraviolet-visible spectrophotometry and scanning electron microscopy

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The study was conducted by applying a 1:1 metal-ligand complexation at pH 3.5, 7.0 and 9.0 whereby $AlCl_3$ and pyrocatechol of the highest purity were used. The Al-pyrocatechol complex was synthesized in the presence of atmospheric pressure at 21 °C for a period of 48 h in total darkness after which the samples were determined by using methods of UV-Vis spectrophotometry and scanning electron microscopy (SEM).



Clearly, pure pyrocatechol is usually colorless in aqueous systems without autoxidation but its color changed completely to a dark cyan as a result of Al complexation. In particular, no visible change to the color of this complex was observed in the experiment conducted at pH 3.5, 7.0 and 9.0. In the UV region of the spectrum, the absorption maxima of pyrocatechol occurred at 212 nm and 275 nm when compared to the metal-ligand spectrum, here the absorption maximum occurred at 278 nm and the absorption intensity increased considerably. In the Vis region of the spectrum, ligand bands from the complex appeared with absorption maxima of 597 nm and 650 nm that conformed to the orange and red light regions. After the addition of auxochromes, a rise of the chromophore system occurred, and it was this effect that determined the shape of the UV-Vis spectrum of the Al-pyrocatechol complex. This compound, shown in its solid state, had a very smooth surface with sharp-edged breakages as presented in the SEM photomicrograph. Primarily, organic substances with o-hydroxy groups showed specific effects on Al chemistry in the environment due to their favorable reaction to Al chelation.

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Occurrence of sursassite in the Lienne valley, Stavelot Massif, Belgian Ardennes

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In quartz veinlets crosscutting the red-purple metapelites of the Otré Formation (Salm Group) in the core of the Lienne syncline, sursassite occurs as orange-red needles associated with manganese oxide masses mostly composed of cryptomelane. Detailed petrographic observation coupled with electron microprobe analytical work reveals sursassite in close association with spessartine, manganoan clinocllore (Schreyer *et al.*, 1986), hematite, and fluorapatite.

The chemical composition of sursassite shows the presence of about 2 wt % MgO, and up to 4 wt % CaO, whereas Fe₂O₃ does not exceed 1 wt %. These substitutions are interpreted in comparison with pumpellyite-(Mg). Heterogeneities have also been detected in the distribution of V and As. From a chemical point of view, these zones rich in V and As correspond to ardennite s.l., previously identified in Bierleux (Pasero *et al.*, 1994).

Sursassite constitutes a new additional phase among the minerals characteristic of the low-grade metamorphism known in the Lienne valley in the western part of the Stavelot Massif, i.e. about 300°C and 1.5kb (Theye *et al.*, 1996). The formation of sursassite, associated with manganoan clinocllore and spessartine, in relationship with quartz veinlets, shows analogies with the formation of carpholite. Due to the presence of about 0.4 Mn³⁺ per formula unit of sursassite, it seems reasonable to consider that sursassite could play the role of carpholite in the more oxidized horizons of the Otré Formation in the Lienne Valley.

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Onset of MORB melting: High-pressure eclogite-facies pegmatites as an example of internal fluid recycling

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Zoisite-bearing high-pressure pegmatites from the Münchberg Massif, Germany, provide an excellent example for the characteristics of the onset of metabasite melting at eclogite-facies conditions. Pegmatites were derived by partial melting of MORB-like eclogite at $T \geq 680^\circ\text{C}/2.3$ GPa to $750^\circ\text{C}/3.1$ GPa, which produced small amounts of tonalitic to trondhjemitic melt. The melt concentrated locally in isolated, small melt pockets and crystallized primary zoisite as liquidus phase at $P \geq 2.3$ GPa/ 680°C to 2.1 GPa/ 750°C . Compositional zoning of pegmatite zoisite records an ensuing multi-stage uplift history with successive, discrete crystallization events at 1.4 ± 0.2 GPa/ 650 to 700°C and 1.0 ± 0.1 GPa/ 620 to 650°C . Resorption textures indicate re-heating and thermal perturbation of the whole system prior to each successive crystallization event. Final solidification of zoisite-pegmatites occurred at 0.9 ± 0.1 GPa/ 620 to 650°C . The data suggest that isolated melt + zoisite crystal mash pockets formed an integral part of the eclogite throughout uplift from melt formation at $T \geq 680^\circ\text{C}/2.3$ GPa to $750^\circ\text{C}/3.1$ GPa to final solidification at ~ 0.9 GPa/ 620 to 630°C ; i.e. over 45 to 60 km. The entire pegmatite-forming process was most likely fluid conserving: Any fluid present during high-pressure melt formation was trapped by fully or nearly water-saturated siliceous melts; due to the small melt fractions these melts did not migrate out of the rock but stayed in isolated pockets within the rock unit; finally, any fluid liberated during pegmatite crystallization interacted with neighbouring, dehydrated eclogite-facies assemblages to form amphibolite-facies hydrous minerals.

Based on average compositions of zoisite-pegmatite, as representative for the tonalitic to trondhjemitic high-pressure melt, and host eclogite, we calculated a set of empirical melt/eclogite partition coefficients. $D^{\text{melt/eclogite}}$ values for Ta, Zr, Hf, Tm, Yb, Lu, V, Sc, Cr, Cu, and Ni range from $D_{\text{Ni}}^{\text{melt/eclogite}} = 0.051$ to $D_{\text{Tm}}^{\text{melt/eclogite}} = 0.7$ and indicate compatibility with respect to eclogite. Rubidium, Ba, Th, K, La, Ce, Sr, Nd, Sm, Eu, Ti, and Tb are moderately incompatible with respect to eclogite and have $D^{\text{melt/eclogite}}$ values between $D_{\text{Rb}}^{\text{melt/eclogite}} = 1.11$ and $D_{\text{Th}}^{\text{melt/eclogite}} = 10.6$.

From microbes to mountains: Molecular signatures of life and its environment

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Biomarkers serve as a rich sources of information about ancient environments and provide important proxy tools for studies of past climatic change. Interpretations of molecular and isotopic signatures are grounded in studies of the habitat and growth of modern analogs to biological sources for ancient compounds. Molecular signatures are rarely simple recorders of material or physical properties (like temperature), and can be influenced by variations in lipid and isotopic properties both within and between organisms. This presentation will highlight two examples of molecular proxies and the importance of ecological and physiological influences on their geochemical record.

The first example underscores the role of ecology on the molecular signatures of modern marine Archaea. Recent studies point to crenarchaeota as important agents in ammonium oxidation, consistent with an apparent affinity of these organisms with deeper habitats and upwelling regions. Archaeal lipid signatures in the modern ocean include inputs from both euryoarchaeota chrenarchaeota, and the relative importance of these inputs can vary with nutrients, especially nitrogen. Ancient archaeal lipid signatures will reflect ecological shifts in regions with variable oceanographic conditions, potentially complicating their utility for temperature reconstruction in such settings.

In the second example, we consider how plant lipids record deuterium abundance in waters in their growth habitat. Large isotopic fractionation associated with lipid biosynthesis can be attenuated by evaporative effects which yield leaf waters enriched in D relative to precipitation. Thus the apparent (or net) fraction between plant lipids and environmental waters reflect both physiological and climatic properties. Understanding of such influences empowers better reconstructions of this emerging proxy for paleohydrologic signatures. We apply such insights to a lipid-based method for reconstructing uplift of the Tibetan plateau and explore implications for understanding tectonic and climatic interactions.

Provenance and genesis of the high Ti heavy mineral sand deposits of South Kerala, SW India: Constraints from CCSEM analysis

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Computer Controlled Scanning Electron Microscopy (CCSEM) is a new fully automated method for the chemical and physical characterisation of the heavy mineral fraction in sands (Frei *et al.*, 2005). For example, CCSEM allows to determine the chemical variation of individual mineral groups (e.g. garnet or ilmenite) and their modal abundance. In this contribution we demonstrate the capabilities of CCSEM for investigating the grade, genesis and provenance of Ti heavy mineral sand deposits.

The world-class heavy-mineral deposits occurring in beach sands around the town of Chavara in SW India are characterized by abundant ilmenite with elevated TiO₂ contents, often exceeding 60 wt. %. In order to determine the provenance and genesis of these high- TiO₂ ilmenite deposits, we have collected a large number of beach sediment samples from an approximately 800 km long stretch of coastline from northern Kerala state to well within the Tamil Nadu state. An additional set of river sediment samples was also taken, roughly covering the areas drained inland from the beach samples. The heavy-minerals in all samples were analyzed by CCSEM, providing both chemical analyses of individual grains as well as the modal composition of heavy-minerals in the sediment. The results show that the sediments in the Chavara high-Ti ilmenite deposits are distinct by minor elements in ilmenite and garnet chemistry as well as heavy mineral assemblage: ilmenite has high MgO and low MnO contents, garnets have low grossular components and the heavy-mineral assemblage is dominated by sillimanite-kyanite in addition to ilmenite. These features correlate with basement geology in the hinterland, and with the results for sediments from rivers, draining the basement. Based on these observations we conclude that high-Ti ilmenite from Chavara beaches is derived from the granulite-facies metasedimentary rocks exposed in the khondalite belt. Our study demonstrates that rapid mineral analyses in sediments by CCSEM is an efficient and powerful new tool for the characterization of mineral compositions and assemblages in sediments, the identification of their possible source regions and thus ultimately for refined exploration for industrial mineral resources.

Reference

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Trace element and isotopic characterization of Neoproterozoic - Paleoproterozoic BIFs (Black Hills, South Dakota, USA) straddling the first rise of atmospheric oxygen between 2.4 and 2.0 Ga

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Banded iron formations (BIF) were deposited in the Black Hills, South Dakota, both prior to and after the first main oxygenation of the atmosphere at ~2.4-2.3 Ga. Paleoproterozoic oxide BIFs deposited before this event still indicate prevalence of reducing conditions in the depositional basins, consistent with the occurrence of stratigraphically associated uranium- and pyrite-rich conglomerates. In contrast, mixed silicate-carbonate-oxide BIFs were formed long after this 2.4-2.3 Ga event, with deposition straddling the end of the ~2.3-2.0 Ga positive $\delta^{13}\text{C}$ anomaly. The older, oxide-facies and detritus-free BIFs were deposited during rifting at ~2.56-2.48 Ga, associated with initial break-up of the Kenorland supercontinent. These BIFs exhibit REE characteristics typical of ambient seawater signatures (positive La, Eu, Y, and negative Ce, anomalies in PAAS-normalized REE diagrams); Sm-Nd model ages of 3.78-2.56 Ga; a high- μ ($^{238}\text{U}/^{204}\text{Pb}$) tenor, typical of the Wyoming craton; and low $^{208}\text{Pb}/^{204}\text{Pb}$ relative $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, implying pronounced fractionation of U relative to Th during source rock weathering processes and (or) during deposition. Deposition of the younger, silicate-carbonate-oxide BIFs appears to have occurred in a rifted continental margin that developed as a consequence of final break-up of Kenorland beginning at ~2.1 Ga, during discrete episodes of rifting precisely dated at 2.02-1.98 and 1.89-1.88 Ga. These horizons of younger BIF both reveal significant detrital input. They also exhibit Sm-Nd model ages of 3.83-2.51 Ga, comparable to the older BIFs. However, the younger BIFs differ by their less-fractionated PAAS-normalized REE patterns, lack of La anomalies, only weakly positive Eu anomalies, and positive Ce anomalies. Positive Ce anomalies may reflect more oxidative scavenging of Ce(IV) onto Fe-oxyhydroxides, generally pointing to a more oxidized seawater environment during their deposition.

Earth's oldest BIFs (Isua, W Greenland) – Constraints from Ge/Si ratios, REE systematics and Sm-Nd and Pb isotopes for different interacting water masses during their formation

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We report trace element, Sm-Nd and Pb isotopic data for individual micro- and mesobands of the Earth's oldest Banded Iron Formation (BIF) from the ~3.7-3.8 Ga Isua Greenstone Belt (IGB, West Greenland) in an attempt to contribute to the characterization of the depositional environment and to the understanding of depositional mechanisms of these earliest chemical sediments. REE-Y patterns of the individual mesobands show features of modern seawater with diagnostic Ce/Ce*, Pr/Pr* and Y/Ho anomalies. Uranogenic Pb isotope data define a correlation line with a slope of 3691 ± 41 Ma, indicating that the U-Pb system remained closed after the formation of this BIF. High $^{207}\text{Pb}/^{204}\text{Pb}$ relative to $^{206}\text{Pb}/^{204}\text{Pb}$ ratios compared to average mantle growth evolution models are a feature shared by BIF, penecontemporaneous basalts and clastic volcanogenic metasediments and are indicative of the ultimate high- μ ($^{238}\text{U}/^{204}\text{Pb}$) character of the source region, an essentially mafic Hadean protocrust. Sm-Nd isotopic relations on a layer-by-layer basis point to two REE sources controlling the arc basin depositional environment of the BIF, one being seafloor-vented hydrothermal fluids ($\epsilon\text{Nd}(3.7 \text{ Ga}) \sim +3.1$), the other being ambient surface seawater which reached its composition by erosion of parts of the protocrustal landmass ($\epsilon\text{Nd}(3.7 \text{ Ga}) \sim +1.6$). Systematic trends in Ge/Si ratios support the above theory and suggest that significant amounts of silica were derived from unexposed and/or destroyed mafic Hadean landmass, unlike iron which probably originated from oceanic crust following hydrothermal alteration by deep percolating seawater.

Long-term turnover of plant derived sugars in soils below natural forest and plantation in Ethiopia

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Background

Carbohydrates are an important pool in the terrestrial carbon cycle. In order to predict future concentrations of CO₂ in the atmosphere, it is crucial to quantify mean residence times (MRT) of carbon species in soils. Furthermore, it is important to investigate which types of land use are suitable for long-term carbon-storage in soils.

Materials and Methods

In our study, we investigated the MRT of plant derived sugars in tropical soils by compound specific isotope analysis (CSIA). Samples were collected in a natural forest dominated by *Podocarpus falcatus* and in an adjacent 40 year old *Eucalyptus saligna* plantation in southern Ethiopia. Contents of Xylose and Arabinose were analyzed via GC-C-IRMS simultaneously with $\delta^{13}\text{C}$ values to one meter depth. [1] The ¹⁴C age of Black Carbon was used for the calculation of MRT in a model, implying advection, diffusion and decay. [2] Calibration of the model was conducted by using a shift in $\delta^{13}\text{C}$ values as a consequence of a change from C₄ to C₃ vegetation in the study area about 600 years ago.

Results and Discussion

MRT of Xylose and Arabinose were the same in the natural forest and the plantation. MRT was exponentially dependent on depth. 70 percent of the sugars had MRT of less than 20 years. Only 1.3 to 2.0 percent of the Xylose and 5.0 to 5.7 percent of Arabinose reached MRT of more than 1500 years. Nonetheless, the *Eucalyptus* plantation contained 33 to 44 percent less sugars down to one meter depth ($p < 0.01$).

Conclusion

The fewer amounts of sugars below *Eucalyptus* should be due to accelerated mineralisation while clear-cutting of the natural forest and reduced litter input after the conversion. Because MRT do not differ between the natural forest and the plantation, the land use with the highest carbon input in the soil should be preferred for carbon-sequestration.

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New method (HR-SF-ICP-MS) to measure biosilica production and dissolution in ocean surface waters

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A new method is described for a accurate and simultaneous determinations of the rate of production and dissolution of biosilica in marine surface waters, using isotopic dilution technique. This technique consists to label diatoms sampled from the euphotic layer with ³⁰Si spike in the form of Si(OH)₄. The samples are then incubated under *in situ* conditions during a given time (usually 24h). The isotopic dilution of the enriched seawater is used to estimate the dissolution of biosilica and the change in the isotopic composition of silica itself is used to estimate its production. Such sampling method and the calculation model associated are described in Corvaisier *et al.* [2005]⁽¹⁾.

In this study we propose to measure the silicon isotopic abundances by a HR-SF-ICP-MS (Element 2) in wet plasma mode instead of TIMS (Finnigan THQ)⁽¹⁾.

In this purpose we apply first an alkaline digestion on biosilica or a preconcentration/subsequent-dissolution using the adapted MAGIC method for the dissolved silicon.

The sample is introduced through a glass concentric nebulizer (100 μ l/min) and a glass jacketed tracey cyclonic spray chamber. Instrumental mass bias is measured with the standard-sample bracketing technique using standards with the same matrix as the sample to avoid the matrix effects. We correct the blank contribution by subtraction of the average of two blanks bracketing the sample. A complete analyse (including standards and blanks) is performed in only 20 minutes. The repeatability and the internal precision on the silicon isotopic abundances of a 100ppb Si solution of a diluted alkaline digestion and diluted preconcentration are better than 1%, similar to the TIMS [1].

This new method is much faster and easier than when using TIMS⁽¹⁾. Moreover because HR-SF-ICP-MS are now widespread instruments it will help to expand biosilica production-dissolution data which are currently very scarce (up to 2003, only 56 published profiles). In fine a better constrain of the silicon budget (production vs. dissolution) in the surface ocean will be gained.

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Hydroxyl contents of deep mantle minerals coexisting with CH₄-rich fluids: Implications for the focusing of fluids in the upper mantle by redox processes

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The high solubility of hydroxyl in nominally anhydrous minerals such as olivine and wadsleyite at high pressures has been used to argue that they may be important hosts for H₂O in the mantle. However, volatiles in the Earth's interior are more accurately described in the system C-O-H where the activity of H₂O is a function of the oxygen fugacity. The oxygen fugacities in the lower regions of the upper mantle and in the transition zone and lower mantle are likely to be quite low and at least 4 log units below the FMQ oxygen buffer. Calculations show that at these conditions a C-O-H fluid will be CH₄-rich. The lower activity of H₂O in the fluid should lower the equilibrium OH⁻ content of coexisting nominally anhydrous minerals such as wadsleyite. Experiments have been performed to study the properties of such reduced fluid phases and examine if they influence the OH⁻ contents of nominally anhydrous mantle minerals at high pressure.

The experiments used a standard double capsule technique with an outer capsule containing a redox buffer (Mo-MoO₂ or Co-CoO) plus H₂O and an inner Pt capsule containing San Carlos olivine or garnet compositions in a graphite liner. Samples were equilibrated between 10 and 15 GPa in a 5000 tonne multianvil press. Results show that at plausible mantle oxygen fugacities minerals such as wadsleyite have H₂O contents over ten times lower than those reported at H₂O saturation. CH₄-rich fluids do not show evidence of having a significant dissolved silicate component. These reduced, low-density fluids should have a tendency to rise out of the deeper mantle and be oxidised to H₂O and CO₂ in the shallow upper mantle. This mechanism may tend to concentrate C-O-H volatiles in the upper mantle, leaving the deeper mantle dryer and with a higher viscosity.

Building Lost City: Serpentinization, mass transfer and life in a peridotite-hosted hydrothermal system

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The Lost City Hydrothermal Field (LCHF; Atlantis Massif, Mid-Atlantic Ridge, 30°N) is the product of reactions between seawater and ultramafic rocks that produce high alkaline (pH 10 to 11), 40 to 90°C fluids that form up to 60m tall carbonate-brucite towers. The fluids are enriched in H₂, CH₄ and other hydrocarbons, produced abiotically through Fischer-Tropsch type reactions, and support dense microbial communities that include anaerobic CH₄- and S-cycling thermophiles. We present an overview of multidisciplinary investigations of the LCHF and highlight the complex interplay between deformation, fluid flow, mass transfer and microbial activity that occur within this long-lived, peridotite-hosted hydrothermal system and the chemical and biological impacts of such off-axis systems on the global ridge system.

Textures and bulk rock chemistries of the harzburgitic serpentinites reflect formation and uplift of a heterogeneous lithosphere in a magma-starved spreading environment, with progressive serpentinization, talc-amphibole metasomatism and veining. Seawater-peridotite interaction at 150-250°C and high fluid-rock ratios (>100 and up to 10⁶) produced enrichments in B, U and light REE, systematic changes in Sr- and Nd-isotope ratios towards seawater values, and highly depleted bulk rock O-, H-, and B-isotopic compositions in the basement. B-isotope analyses of the fluids and hydrothermal precipitates indicate that brucite is a significant, temporally variable, reservoir for Mg and B in these systems.

High fluid fluxes have important implications for S- and C-cycles: sulfur geochemistry indicates a loss of primary sulfide, an uptake of seawater sulfate, and local microbial remediated sulfate reduction and sulfide oxidation in the basement. Our studies show that the total carbon stored in the serpentinites is dominated by hydrocarbons and suggest that serpentinites may represent an important, as yet unidentified, reservoir for dissolved organic carbon from seawater. We conclude that high seawater fluxes and the interaction with both variably fresh peridotites and pervasively serpentinized peridotites is crucial to the formation of volatile-rich Lost City-type systems and that transform-related normal faulting and mass wasting in the south of the massif facilitates seawater penetration necessary to sustain hydrothermal activity over tens of thousands of years.

Prevention of asbestos floating from outdated construction materials

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Approaching Crisis

Human beings have used a huge amount of asbestos since the stone age because of its good spinnability in the beginning and then because of good physico-chemical properties in industrialized nations. Asbestos is frequently used in construction materials, and they should start to fly as extremely fine fibers many years after they are used and when the construction materials are worn out. The fiber is believed to cause especially *malignant mesothelium* and other related diseases.

How to Cope with the Problem

Special reagent (Patent pending) has been invented to prevent asbestos floatation into the air. The reagent has high affinity with all kinds of asbestos and envelopes them when it is sprayed on the asbestos-containing materials. Once it envelopes asbestos and dried up, it is hardly possible to separate the reagent from asbestos. Among the asbestos, crocidolite asbestos is the most tough one and we treated crocidolite with the reagent. Then we leached it by strong sulfuric acid (1.8M) for more than 96 hours. The reagent-treated asbestos are then pulverized under 400 micron. Each fine fiber of crocidolite asbestos is entirely enveloped by the solidified reagent. As long as we observed them under the phase contrast microscope, we can hardly identify crocidolite. Using a highly efficient XRD, the crocidolite can be identified.

Conclusion

We of course prefer to recycle as many kinds of materials as possible. However, we may not be able to recycle asbestos at all. On the contrary, we prefer asbestos-free atmosphere. When houses, buildings, facilities and their equipment are reconstructed or repaired, fine asbestos fibers may start to fly even if the construction materials are not yet worn out. Therefore, somehow floatation of fine asbestos fibers have to be prevented. We are going to show how the reagent works to prevent floatation of fibrous asbestos.

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Mass transfer by fluid and duration of oxygen isotope exchange during contact metamorphism at Hirao-dai, Japan

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A reaction zone between a metamorphosed basic dyke (MB) and marble at Hirao-dai, north Kyushu, Japan, consists of well-organized sequential zones of diopside, garnet and wollastonite; textures are characteristic of diffusion-controlled structures. The reaction zone formed during contact metamorphism associated with intrusion of a Cretaceous granodiorite at about 300 MPa and 700°C (Fukuyama, *et al.*, 2004). The MB consists of diopside, biotite and plagioclase ($X_{Ab}=0.4-0.8$), whereas the marble is almost pure calcite.

Minimum estimate of time-integrated flux forming a reaction zone is 3.46 mol fluid/mol reaction zone: 1.29 mol fluid/mole as reactive fluid and 2.17 mol fluid/mol as non-reactive fluid. 1mol of reaction zone consists of 0.42 mol diopside, 0.11 mol garnet, and 0.48mol wollastonite from overall reaction: $0.07K_{2.00}Mg_{3.89}Fe_{1.42}Al_{2.48}Ti_{0.16}Si_{5.82}O_{20}(OH)_4 + 0.02Na_{0.64}Ca_{0.36}Al_{1.36}Si_{2.64}O_8 + 0.05CaMg_{0.77}Fe_{0.23}Si_{2.00}O_6 + 1.15CaCO_3 + 1.09SiO_2 + 0.03FeO \square 0.02AlO_{3/2} = 0.42CaMg_{0.72}Fe_{0.28}Si_2O_6 + 0.11Ca_{2.86}Fe_{0.14}Al_{2.00}Si_{3.00}O_{12} + 0.48CaSiO_3 + 0.01TiO_2 + 0.01NaO_{1/2} + 0.14KO_{1/2} + 0.14H_2O + 1.15CO_2$. This estimate is based on the mineralogical evidence and steady-diffusion modelling (Fukuyama *et al.*, 2006).

We measured ¹⁸O and ¹³C of calcite along a line segment perpendicular to the reaction zone-marble boundary. ¹³O composition isn't change, but ¹⁸O composition changes in proportion to distance from the reaction zone-marble contact. This shows that ¹⁸O is strongly fractionated between CaCO₃ or CO₂ and H₂O because mineral reactions may buffer the CO₂-H₂O content of fluid.

The duration of oxygen isotope exchange (*t*) can be calculated from effective diffusive width (*W*) and diffusive coefficient of oxygen in calcite (*D*) using the following equation: $W^2=2Dt$

The minimum estimated duration of oxygen isotope exchange is 357 m.y. We interpret this duration is the same as the duration of reaction zone formed, giving the fluid velocity 5.3×10^{-11} m/s.

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Thermochemical coupling in deep mantle plumes: A case study of Turkana, N. Kenya

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Subducted oceanic crust forms the likely source for a dense and more fertile layer at the core-mantle boundary. Numerical modeling predicts that entrainment of this dense material by an upwelling thermal plume will result in episodic volcanism occurring at episodic intervals on time scales of several to hundreds of millions of years (Lin & van Keken 2005).

Our study of 40 my of mafic eruptive activity in Turkana, Kenya reveals volcanological and geochemical features that are fully compatible with the numerical models, suggesting that magmatism in this part of the East African Rift System reflects deep entrainment of recycled oceanic crust by a thermally-driven plume. Volcanism at Turkana occurred in three distinct pulses separated by several million years each. No flood basalt province typical of strictly thermal plume head volcanism is associated with any of the pulses. The most voluminous pulse (26-16 Ma) led to rift propagation to both north and south, with fault growth and new rift basin development. Episodic volcanism is also reported from Samburu, Kenya, 200 km to the south (Tatsumi & Kimura 1991) and 100 km to the north in Ethiopia (George *et al.* 1998) in each case subsequent to peak Turkana episodes. These features contrast with observations in Afar, where plume head volcanism occurred 30 Ma and modern basalts are erupted along extensional features in the rift axis.

Mafic lavas from the major episode in Turkana – including abundant picrites – are geochemically distinctive. They have Sr-Nd-Pb-He isotopic signatures characteristic of high- μ ocean island basalts, and olivine Ca, Ni contents indicative of a pyroxenitic source (Sobolev *et al.* 2005, Herzberg 2006). We postulate that entrained fertile pyroxenite has been a source of mafic volcanism at Turkana.

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Impact-generated ultrafine particles of olivine and serpentine suggesting a source of aerogels in the air of the early Earth

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Intense impacts of meteorites on to early oceans have been suggested in the period of Late Heavy Bombardment [1, 2]. The mechanism of oceanic impact is different from that of subaerial impact. The oceanic impacts generate Ultrafine Particles (UPs) [3] and have possibility to generate a large amount of UPs of serpentine. However, few experimental investigations of impact-serpentinization exist. The UPs formation following impact explosion might influence the environment of the early Earth.

We performed shock-recovery experiments using a single-stage propellant gun to simulate simple ocean impact events of meteorites. The samples are powder of olivine with and without water in steel sample container. The products were analyzed with XRD, SEM and TEM.

SEM observation shows the formations of UPs of metal oxides. In addition, TEM observation shows the formation of UPs of olivine with different compositions from the starting one, serpentine and brucite. The grains of such UPs were some hundreds of nanometres in size.

Formation of UPs was unexpected from our impact experiments because the experimental conditions were far below the theoretical vaporization and/or melting conditions of starting materials. Here we propose that the presence of water significantly promoted the conversion of samples into UPs. The UPs formation by oceanic impacts may influence the change of Earth's environment such as generating aerosol and shielding sunlight.

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Sulfide oxidation, acidification and deoxygenation by reaction of resuspended sulfidic benthic sediments.

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Black, gel-like, benthic sediments with high acid volatile sulfur (AVS) concentrations (1-6% dry mass) are common in waterways affected by acid sulphate leachate. These sediments are often called monosulfidic black ooze (MBO). Floodwater re-suspension of MBO has been implicated in massive fish kills associated with severe deoxygenation and acidification of coastal lowland rivers. This study examines changes to sediment and water chemistry during laboratory experiments designed to simulate flood-induced sediment re-suspension events. Re-suspension of MBO in water decreased dissolved oxygen from 7.70 mg.L⁻¹ to 0.86 mg.L⁻¹ within 1-2 minutes. The oxidation of the acid volatile sulfur fraction in the MBO resulted in the rapid formation of elemental sulfur. pH remained near-neutral during this oxidation step. It was 4 days until the elemental sulfur began to oxidise, causing acidification (pH <3.5). Metal concentrations within the MBO material were within sediment quality guidelines. However, the oxidation of AVS and acidification of the MBO material mobilised metals to the water column at concentrations greatly exceeding the recommended water quality guidelines. The current sediment quality guidelines for metals can be a poor estimate of the environmental risk, particularly as show here for sediments that contain elevated acid volatile sulfur contents.

Fe, Co and Ni in Ureilites: Metal-silicate equilibration in the UPB

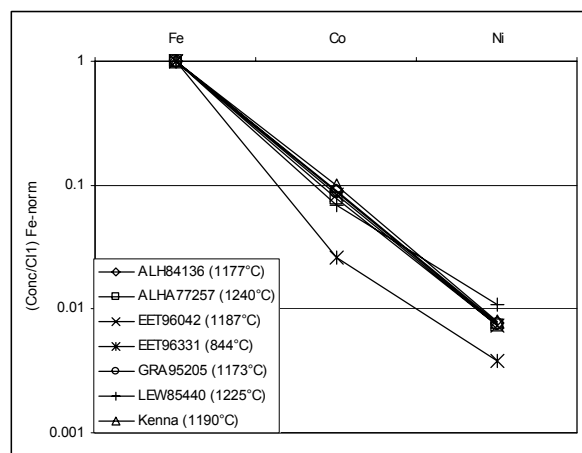
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Ureilites are coarse-grained olivine- and pigeonite-bearing achondrites with carbon-rich material occurring along grain boundaries [1]. It is suggested that Ureilites represent asteroidal mantle restites [2].

In this study we present Fe, Co and Ni concentration data of olivine from eight Ureilites with different Fe-contents, ranging from 8 to 22% *fa*. Measurements have been conducted by means of LA-ICP MS at the University of Göttingen.

Starting from a CI1 composition we calculated a model core compositions for each Ureilite. With the equations taken from Seifert *et al* [3], we calculated the Co and Ni content of olivine that equilibrated with metal of the model core composition at temperatures ranging from 1000°C to 1500°C. These data are compared to measured Ureilite olivine compositions. Our data give olivine-metal equilibration temperature of about 1185°C. Exceptions are LEW85440 and ALHA77257 which show a higher equilibration temperatures of ~1230°C. EET96331, which is very low in Co and Ni compared to Ureilite olivine with similar Fe-content, gives a significantly lower equilibration temperature of ~800°C.



Ureilite olivines seem to have been equilibrated with a metal with a composition similar to the core of the UPB. Except for EET96331, equilibration temperatures range from 1173 to 1240°C, which is broadly in agreement with olivine-pigeonite thermometer data published by Singletary *et al.* [4]. The Fe-, Co- and Ni-composition of the Ureilite olivine has been established during metamorphism. This has implications for future Fe-Ni-isotope relative age dating, which is in progress.

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