

Surface complexation of Uranium(VI) on Fe/Mn (hydr)oxides

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The fate and mobility of U in oxic soils, groundwater and the marine environment is controlled by sorption of UO_2^{++} onto nanocrystalline iron and manganese (hydr)oxides. Thermodynamic models for such reactions are needed before we can understand the aqueous geochemistry of U. However, we cannot develop useful thermodynamic models until we have a molecular-level understanding of U sorption and complexation. Previous EXAFS studies of UO_2^{++} sorption on FeOOH have been interpreted as indicating an inner-sphere $>\text{Fe}(\text{OH})_2\text{UO}_2$ surface complex formed by edge sharing with FeO_6 polyhedra (²E complex). However, this complex is at odds with the known surface site densities of FeOOH phases. On goethite, for example, ²E complexes can only occur on the {210} and {010} planes (space group setting Pnma) which comprise only a small fraction of the surface area. Here, we show that previous EXAFS spectra have been misinterpreted owing to the neglect or incomplete inclusion of multiple scattering. The dominant UO_2^{++} surface complex on FeOOH is $(>\text{FeOH})_2\text{UO}_2(\text{H}_2\text{O},\text{OH})_3$ and $(>\text{FeOH})_2\text{UO}_2\text{CO}_3$ (²C complex) resulting from bidentate corner-sharing with two adjacent FeO_6 surface polyhedra. Ab initio calculations of U-O and U-Fe distances in the (²C) complexes are consistent with the EXAFS results. On goethite, ²C complexes can form on the {101} planes which comprise nearly all of the reactive surface area; the 2C complex explains the high sorption capacity (>2 wt%) for U(VI) on goethite and, apparently, ferrihydrite.

We developed a surface complexation model to fit a series of sorption experiments of U on goethite and ferrihydrite. Using a 1pK formalism and Basic Stern model for electrostatics, we found we could fit our data using $(>\text{FeOH})_2\text{UO}_2(\text{OH})$ and $(>\text{FeOH})_2\text{UO}_2\text{CO}_3$ (²C) complexes, consistent with EXAFS results. An analogous model for U sorption onto hexagonal birnessite was developed using the $(>\text{MnO})_3\text{UO}_2\text{OH}$ and $(>\text{MnO})_3\text{UO}_2\text{CO}_3$ complexes assuming that UO_2^{++} complexes over vacancies in the phyllosomanganate layer. Implications of our models for the fate of U(VI) in soils and aquatic environments will be discussed.

The Os isotope heterogeneities in the mantle sequence of the Bangong Lake ophiolite, northwestern Tibet

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Two type harzburgites occur in mantle sequence of the Bangong Lake ophiolite, NW Tibet. Type I is Cpx-bearing harzburgite with $\text{Cr}^\# = 20\sim 25$ of spinel reflecting 10~15% degrees of partial melting; Type II is Cpx-free harzburgite with $\text{Cr}^\# = 69\sim 73$ of spinel representing 35~40% degrees of partial melting formed in the suprasubduction zone (SSZ) [1]. In Type I, the $^{187}\text{Os}/^{188}\text{Os}$ ratios (0.12446 to 0.12853) are chondritic and the $^{187}\text{Re}/^{188}\text{Os}$ ratios (0.44 to 1.77) are suprachondritic reflecting that Re gain recently by basaltic melt percolating during the formation of the Bangong Lake crust 167 Ma ago [2], while in Type II, part of $^{187}\text{Os}/^{188}\text{Os}$ ratios (0.12166 to 0.12896) are subchondritic, this can be explained by Re depletion during ancient partial melting. The old Os isotope model age (>950 Ma) of one Cpx-free harzburgite in a young ophiolitic mantle show that ancient Os isotopic heterogeneities can survive in the Earth upper mantle.

Osmium concentrations tend to decrease from Type I (Cpx-bearing harzburgites, 5.25-5.45ppb) to Type II (Cpx-free harzburgites, 4.4-4.45ppb, one sample is 1.32ppb) indicating that Os does not behave compatibly during melt percolation as it is observed during partial melting, but becomes dissolved and mobilized by the percolating melt [3]. But the heavy serpentinization likely caused the Os loss by the sulphide decomposition in a SSZ environment with high $f\text{O}_2$.

This study shows that Type I and II harzburgites of the Bangong Lake ophiolitic mantle have complex and different evolution. However, the Os isotopic features are consistent with a model where the two type harzburgites belong to the same melting regime producing the Bangong Lake oceanic crust. This scenario is also observed early in Troodos ophiolite [3].

Acknowledgment

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Genesis of tholeiitic and calcalkaline series of Zao volcano, NE Japan arc, Japan

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Genesis of co-existing tholeiitic series (TH) and calcalkaline series (CA) in island arc and their relationship has been a focus of attention because it is critical to understanding magma genesis in island arc. The Zao is Quaternary volcano situated on the Tohoku Backbone Ranges, Northeastern Japan arc, and both of TH and CA co-exist in continuous volcanic activity (Sakayori, 1991). We investigated the Sr, Nd, Pb isotope and trace element compositions to discuss genesis of TH and CA from Zao volcano.

The trace element compositions of the studied samples show the typical characteristics of island arc magma in the diagram of MORB normalized pattern, such as enrichment of LILEs and negative Nb spike. Positive Pb and Sr spikes are also apparent. The LILEs enrichment and negative spikes of Nb are relatively larger in CA than TH. Although abundance ratios of Cs/Nb of TH are restricted to 0.09 - 0.20, those of CA can be divided into two ranges, such as 0.20 - 0.25 and 0.42 - 0.57.

The isotopic compositions of TH are more enriched compared to CA. In all the diagrams presenting the relationship of the isotope compositions, TH and CA make different linear trends, which indicate the mixing relation. Furthermore, Pb isotopic compositions suggest that two depleted endmember is necessary to explain the trend of TH and CA. The depleted endmember of TH is relatively enriched than that of CA. On the other hand, two enriched endmembers are required from the relationships between parent/daughter and the isotope ratios, because TH and CA show different linear trends in those relation and the linear trends are diverse in the direction of isotopically enriched side. The both of the enriched direction of TH and CA is differ from the mixing trend of mantle wedge and recycled materials from subducting slab observed from Northeastern Japan (Shibata and Nakamura, 1997). From the observations in the above, it can be concluded that four components are necessary to explain the chemical characteristics of TH and CA from Zao volcano and the different two enriched components are derived from different crustal materials, although the sources of those are not obvious yet.

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Anthropogenic contamination of bivalves revealed by Cd isotopes

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We are studying Cd isotopic compositions in bivalves to assess their natural and anthropogenic variability and sources. Oysters (*Crassostrea gigas*) from BC were collected from Desolation Sound (BC coast) and Barkley Sound (west coast of Vancouver Island). For comparison, we analyzed bivalves collected off the coasts of France, oysters (*C. gigas*) from the Gironde estuary and northern Brittany and mussels (*Mytilus galloprovincialis*) from the Gulf of Lion.

Cd isotopes were measured by dynamic multi-collection using a Nu Plasma MC-ICPMS and sample-standard bracketing technique together with external normalization to correct for instrumental mass bias. Results are reported in δ notation (δ), normalized to a mass difference of one atomic mass unit. Our reference Cd standard (High Purity Standards, Inc., lot 291012) has the same Cd isotopic signature as JMC Cd [1,2]. Reproducibility is estimated from repeat analysis of a secondary Cd standard (High Purity Standards, Inc., lot 502624), 0.37 ± 0.03 permil/amu (2SD; n=31).

BC oysters have Cd isotopic signatures consistent with those reported for seawater from the N Pacific [3,4] suggesting that the high Cd concentrations (4.8-15.8 ppm tissue dw) found in bivalves along this coast result from natural coastal upwelling. Oysters from the BC coast have a slightly lighter signature than those from the west coast of Vancouver Island, potentially resulting from a larger anthropogenic contribution consistent with this geographical location. Mediterranean mussels have Cd isotopic signatures within the range of NW Mediterranean seawater values [3]. Oysters from northern Brittany and the Gironde estuary have signatures significantly lighter than the literature value for the Atlantic [4]. The Gironde oysters have the lightest signatures consistent with pollution resulting from industrial evaporation-condensation processes, as documented by the shift to $\delta = -0.16$ permil/amu for two dust samples from a Pb-Zn refinery plant in northern France [2]. These results demonstrate the ability of Cd isotopes to trace anthropogenic pollution.

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Geochemical variation and residence time of groundwater in Mt. Fuji area, central Japan

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Many groundwater samples were collected from Mt. Fuji area, central Japan which is totally composed of basaltic materials. The samples were analyzed for Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Si , Al^{3+} , Fe^{2+} , Fe^{3+} , TC (total dissolved carbon), Cl^- , NO_3^- , SO_4^{2-} and TP (total phosphorus). Analytical data plotted against altitude indicate that alkali and alkali earth element (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ca^{2+}) and Si concentrations increase with decreasing altitude, indicating that the dissolution of silicates in basaltic materials control the trends. Ca and Mg concentrations positively correlate with each other and the correlation coefficient is 1.64. This is consistent with CaO/MgO molal ratio of basalt which is 1.47. Therefore, it is inferred that Ca and Mg in groundwater were derived mainly from the congruent dissolution of basalt. Ca/Si concentration ratio determined by the dissolution reactions of basalt accompanied by the precipitation of allophane is 0.29 which is lower than 0.48 estimated from the analytical data on groundwater. This lower value could be due to the precipitation of silica mineral (SiO_2). The agreement between theoretical and analytical results indicate that Ca, Mg and Si concentrations of groundwater are governed by dissolution and precipitation reactions. In order to interpret groundwater chemistry and estimate residence time of groundwater the simplified coupled dissolution kinetics-fluid flow model was used. Assuming reasonable values of parameters (reactive surface area, mass of groundwater, temperature etc) and using rate constant experimentally determined, residence time of groundwater in southeastern part of Mt. Fuji area (Kakitagawa site) was estimated to be several years to 30 years. This estimated residence time is consistent with isotope data (helium isotope and tritium concentration).

CO₂-water-basalt interactions: Experimental and mineralogical study

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Introduction

Development of a better understanding of fluid-rock interaction is important in many areas of applied science and basic research. Investigation of reaction of basalt with H_2O and CO_2 at different P-T-fO₂ conditions is important both for planetary processes including processes in subduction zones of the Earth and mineral storage of CO_2 including the problem of reducing the anthropogenic CO_2 emission into the atmosphere. We have carried out experimental, mineralogical and carbon stable isotope study of this reaction.

Experimental Method

Carbonation experiments were run by exposing natural basalt powders (100-200 μm grain size) to CO_2 and H_2O under various conditions in a hydraulic press (total pressure 1 kbar and 400-500°C). Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was used as a source of CO_2 and H_2O . Additional amounts of H_2O were added in the platinum capsules. The thus produced CO_2 and H_2O were then reacted with the basalt powder at high pressure and temperature. Gas phase and solid products of experiments were analyzed by manometry, step heating and mass-spectrometry techniques. Mineralogical study of the products of experiments by Scanning Electron Microscopy allowed the identification and observation of carbonates and water-bearing minerals.

Discussion and Conclusions

Our experimental results document the effect of the H_2O - CO_2 medium on basalts under these P,T conditions and that calcite forms during the carbonation of plagioclase. We observed that carbonation reaction in basic rocks is different from that in ultrabasic rocks. Pressure, temperature and molar fractions of H_2O and CO_2 are important parameters whose influences were quantified. Measured $\delta^{13}\text{C}$ of gas and solid phase allowed to discuss kinetic and thermodynamic factors of carbon isotope fractionation in such reactions and are discussed in terms of mass balance.

A study on the formation mechanism of Temagami Iron-Formations, Canada

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In order to elucidate systematically the formation mechanism of BIF (Banded Iron-Formations), a BIF sample collected at Temagami, Canada was characterized by optical microscope, EPMA, Xray microscope, SIMS, and chemical analysis. This BIF can be divided into three layers visually; black layer, white layer, red layer. Main minerals in the three layers were magnetite, dolomite and quartz with fine hematite particles respectively.

To estimate the formation temperature of each three mineral and the formation environment (especially oxidation-reduction conditions), the oxygen isotope ratios (¹⁸O/¹⁶O) and contents of rare earth elements were measured by SIMS and chemical analysis. The isotope equilibrium temperature of dolomite and magnetite located in the white layer were 250-350°C. In the rare earth elements patterns for all the layers, a positive Eu anomaly appeared suggesting contribution of the anoxic submarine hydrothermal fluid for the formation of the BIF. On the other hand, a negative Ce anomaly, which indicates a character of oxic sea water, was observed for a part of samples of the red layer. These dolomite and magnetite may be formed under reduction conditions at high temperature, that is, from mixed water of the large amount of anoxic hydrothermal water of 250-350°C and the small amount of oxic sea water. While magnetite and dolomite located in the black layer shows lower formation temperature of 100 °C than that of magnetite and dolomite in the white layer. The latter magnetite and dolomite may be formed from hydrothermal water with high mixing percentage of seawater.

As mentioned above, each mineral in the layers might be precipitate from the fluids formed by mixing of large amount of anoxic submarine hydrothermal fluid with high temperature and small amount of oxic seawater with low temperature. The mixing degree may be different among minerals in the BIF.

High-grade Ag-Cu-Sn-In mineralization in the Nishizawa-Ashio area, Tochigi Prefecture, central Japan

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Mineral Identification and Observation

Polymetallic (Au-Ag-Cu-Pb-Zn-Fe-As-Sb-Bi-Sn-In-W) vein-type mineralization in the Nishizawa-Ashio area occurs in strongly altered late Neogene felsic volcanic rocks. Recently Ishihara (2006) and Ishihara *et al.* (2006) reported that indium had been exploited in ore concentrates (e.g., 1200 tons In at Ashio). At Nishizawa, roquesite and "sakuraiite" (CuZn₂InS₄) were identified as discrete In minerals, associated with Pb,Se-bearing matildite, electrum (Au:Ag≐ 5:5-7:3), chalcopyrite, sphalerite (1-2% FeS), cassiterite and quartz. Canfieldite-argyrodite, Se-bearing acanthite, proustite-pyrargyrite, Ag-bearing tetrahedrite-freibergite (Cu:Ag=5.4:4.6-4.2:5.7), smithite and ferbeite (Fe:Mn≐ 9:1) are also observed. Roquesite frequently occurs as radiating prismatic crystals (up to 0.5 mm), and sometimes as intergrowths with "sakuraiite".

Conclusions

In-bearing sphalerite as solid solution between sphalerite and roquesite has been previously reported (e.g., Burke and Kieft, 1980). The roquesite-"sakuraiite" intergrowths at Nishizawa reveal no solid solution between roquesite and sakuraiite, and instead imply that In-bearing sphalerite represents solid solution between sphalerite and incompletely defined "sakuraiite" (with petrukite as an intermediate phase?).

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Geochemical study on Bousei, Hotta and Smetanin Seamounts near the Japan Trench in Northwestern Pacific Ocean

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The Northwestern Pacific plate is characterized by existence of a large number of seamounts (Koppers *et al.*, 1998). It is widely accepted that these seamounts were produced by extensive magmatic activity during the Cretaceous in the South Pacific that is considered to be one of the largest volcanic events in Earth's history. As this magmatism would represent large-scale mantle upwelling, the magmatism could provide a key constraint to understand chemical evolution of the Earth. Due to this importance, many researches have been conducted on the south Pacific islands, and thus present-day magmatism in the South Pacific is well constrained. In contrast, little constraint has been given to the past volcanic activity in this region.

It has been reported that there are two peaks in the volcanic activity in the South Pacific during the Cretaceous (after Winterer, 1976). As the volcanic peaks should be essential to understand the large mantle up-welling, an investigation on the volcanism during the Cretaceous should be important. The Cretaceous age seamounts near the Japan Trench (e.g., Takagi *et al.*, 1989) are thus suitable examples to study the magmatism in the South Pacific. For the evaluation of the origin of these seamounts, we collected samples from these seamounts during Geological Survey of Japan Daini-Hakureimaru cruise. Drilling and dredging were conducted at 12 sites and fresh samples, alkali basalts and andesites, were recovered from three Seamounts; Bousei, Hotta and Smetanin Seamounts. The phenocrysts are mainly plagioclase and pyroxene with/without hornblende. The geochemical character of the rocks from the Bousei and Hotta are HIMU-type. In contrast, those from the Smetanin show less HIMU signature. In this presentation, we will discuss the origin of Seamounts along Japan Trench and constrain the volcanic activity in the South Pacific.

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The influence of Philippine Sea Plate on the composition of mantle beneath Kyusyu, SW Japan arc: Along-arc variation of B data

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Volcanism in Kyusyu island is associated with subduction of Philippine Sea Plate (PSP) under Eurasian plate. Kyusyu-Palau Ridge, which subducts nearly at right angles to central part of Kyusyu, marks the boundary between young (15-26 Ma) PSP in the north and old (37-115 Ma) PSP in the south. Thus volcanic rocks from Kyusyu are good samples to test the compositional difference resulting from the subduction of oceanic plates with different ages.

We studied the difference in subduction component using boron element. As boron is enriched in altered oceanic crust and ocean sediment, it is one of the best indicators to show the contribution of fluid phase coming from the subducting plate to the mantle beneath volcanic arc. The release of the fluid phase from the oceanic plate is believed to occur in two manners. One is by aqueous fluid at high temperature, and the other is by the dehydration process, i.e. the breakdown of hydrous phases at high pressures. In this case, fluid is continuously released from the plate with increasing pressure, because various phases were involved in producing boron-rich fluid at different pressures.

The ratio of B/Nb was used to see the contribution of the subducting plate. It eliminates the influence of different degrees of partial melting in the mantle and fractional crystallization and crustal contamination in the crust.

The across-arc variation as observed by B/Nb ratios in volcanic rock is almost absent in the northern Kyusyu (NK), whereas it shows a gradual decrease in B/Nb from the volcanic front to the back-arc side in southern Kyusyu (SK). In addition, the B/Nb ratio of rocks from the volcanoes at the volcanic front is relatively high in the SK (~7.5), whereas it is relatively low in the NK (~3.5).

The lack of lateral variation in subduction component in volcanic rocks from the NK indicates a possibility that the release of fluid phase is completed before the oceanic plate reaches the volcanic front. The relatively low number in B/Nb ratio also supports this hypothesis. The young age of oceanic plate suggests a high temperature gradient in the depth profile of the subducting plate. In contrast, the volcanic rocks from the SK show a normal across-arc variation of subduction component typically related with the subduction of relatively old and cold oceanic plate.

Oxygen and sulfur isotope characteristics of the Salmagora Complex, Kola Peninsula

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Introduction

Oxygen and sulfur isotope study on the rock of dunitewehrlite-melilitolite (type 0) from the early stage of magma differentiation and on the rock of pyroxeneite-ijolite (type 1 and type 2) from the later stage, which are classified based on the mineralogical and geochemical characteristics, is performed for the contribution to the petrogenetic model of the Salmagora ultramafic-alkaline-carbonatite complex in the Kola Peninsula.

Experimental Method

25 bulk rock samples were analyzed for oxygen isotope using silicate oxygen preparation line and Finnigan MAT 252 mass spectrometer in Indiana University and splits of the samples used for oxygen isotope were also analyzed for sulfur isotope composition by CF-mass spectrometer.

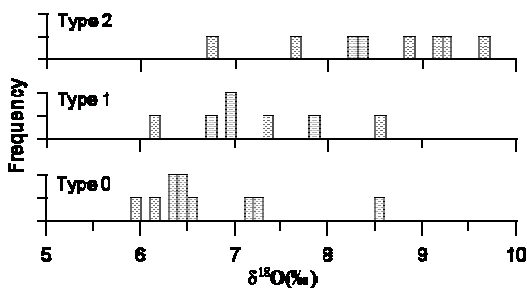


Fig. 1. Variations of oxygen isotope compositions of the Salmagora Complex.

Results and Discussions

In Figure 1, we can observe that oxygen isotope composition systematically increases from type 0, type 1 and to type 2. Especially each rock type of pyroxenite, melteigite, ijolite and urtite in type 2 has higher value than that in type 1 by +0.6 to +2.4‰. Sulfur content was below analytical limit in type 0. The isotope composition varies from -9.3 to -4.8‰ for only melteigite in type 1 and from -4.2 to +1.0‰ in type 2. The increases in oxygen isotope composition from type 0 to type 1 can be explained by common magmatic differentiation process [1] with the influence of crustal contamination, while type 2 seems to indicate another highly evolved magma. Similarly, the low sulfur isotope values in type 1 may also be the effect of crustal contamination and the higher values of type 2 indicates the effect of more evolved magma.

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Inorganic arsenic speciation in contaminated soils, in Korea

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Materials and method

The selected site for this study is an area of arsenic contaminated region (abandoned mine) and near land.

Total arsenic concentration in soil samples and reference materials were as follows. 0.1g of sample was accurately weighed into acid washed digestion vessels containing 9ml of HCl and 3ml of HNO₃, and the resultant solution was heated at 140°C for 1hr in a digestion block. The solutions were allowed to cool and then diluted to 100ml with deionized water. The extraction of the arsenic species for speciation analysis were as follows. 0.1g of soil sample and 15ml of extractant (1M of phosphoric acid + 0.1 M of ascorbic acid) were reacted in a microwave system (Milestone 1200 Mega, power 60W, 15min). This solution is then cooled at room temperature and centrifuged at 2500 rpm for 30min. Total arsenic and arsenic speciation of the supernatant solution was analyzed by ICP-AES and SPE-HG-ICP-AES respectively.

Result and discussion

Total arsenic concentration in samples were measured between 109.97 and 11758.31ppm. In all samples, the majority of arsenic was present as AsV, while AsIII only account for < 3% of the total arsenic. The extraction efficiency, relative to the total arsenic concentration, varied from 25 – 108%. Most of the samples - except to one samples - showed recovery efficiency of above 86%. Only one samples exist both AsIII and AsV and recovery efficiency is not good (respectively 3.18% (AsIII) and 22.18% (AsV)). This sample is tailing which is mostly composed of calcite mineral. Concentration of the Ca is about 24%. AsIII of the tailing sample is presumed to be adsorbed on the calcite surfaces.

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Minor and trace element geochemistry of a branching coral *Acropora* sp. skeleton

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Incorporations of chemical elements and isotopes, into coral skeletons are influenced by ambient water conditions which may provide important information on past climate in the tropics. The geochemistry of *Acropora* is significantly important for the past-temperature reconstruction because *Acropora* is one of the main genera constituting the coral reefs. *Acropora* may also provide unique opportunity to evaluate the effects of physiological processes on the elemental incorporation. Branching coral *Acropora* consists of fast-growing axial corallite and slowly growing radial corallite at the visible scale. On the other hand, at the micro-scale, there are several types of skeletal elements precipitated under different biological mechanisms. However, geochemistry of branching corals has not been well understood. To investigate the mechanisms of elemental incorporation into *Acropora* skeletons, chemical and isotopic compositions in the skeleton were analyzed at various spatial resolutions.

The chemical profiles of both axial and radial corallite along with growth axes were measured by conventional ICP-MS and Stable Isotope Mass Spectrometry. The tip and basal parts of *Acropora* skeletons were also analyzed at micro-scale. The Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca ratios were measured in ~8µm diameter spots by using NanoSIMS, and Mg, Sr, Ca, and S distributions were analyzed by Electron Probe Micro Analyzer (EPMA), with a spatial resolution of ~2µm.

Based on the elemental distribution obtained by EPMA, we found that the *Acropora*'s skeleton is composed of more than three types of the skeletal elements, "Framework", "Infilling" and "High-Mg Low-S" skeletons. Observation of skeletal structure revealed that the skeletal porosity decreased with distance from the tip, because "Infilling" skeletons possibly filled the space between "Framework" skeletons. Micro-scale elemental analyses (EPMA and NanoSIMS) revealed that "Infilling" skeletons have lower Mg/Ca and higher Sr/Ca and U/Ca than "Framework" skeletons. Since the "Infilling" skeletons were probably formed under the slower calcification rate than "Framework" skeletons, the elemental fractionation pattern between two skeletal elements is consistent with the model of elemental incorporations dependent on calcification rate. The chemical profiles of axial corallite along with the growth were significantly affected by the proportions of "Infilling" skeletons.

Mantle and crustal processes in the Hadean and Archean: Evidence for the onset of subduction at 3.8 Ga

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Considerable geochemical evidence supports initiation of plate tectonics on Earth shortly after the end of the Hadean. The present upper mantle retains old heterogeneities, some of which likely derive from subduction in the early Eoarchean. Nb/Th and Th/U ratios of mafic-ultramafic rocks from the depleted upper mantle begin to change from 7 to 18.2 and 4.7 to 2.9 (respectively) at 3.6 Ga. This signals the appearance of subduction-altered slabs in general mantle circulation from subduction initiated at 3.8 Ga. Juvenile crustal rocks begin to show derivation from progressively depleted mantle with typical igneous $\epsilon_{Nd}:\epsilon_{Hf} = 1:2$ after 3.6 Ga. Cratons with stable mantle keels that have subduction imprints begin to appear at 3.5 Ga. These changes all suggest that extraction of continental crust by plate tectonic processes was progressively depleting the mantle from 3.6 Ga onwards. Neoproterozoic subduction appears largely analogous to present subduction except for the production of large cratons with thick mantle keels. The earliest Eoarchean juvenile rocks and Hadean zircons have compositions that reflect the integrated effects of separation of an early enriched reservoir and fractionation of perovskite from the Mars-sized, impact-derived magma ocean, rather than separation of voluminous continental crust or oceanic plate tectonics. Hadean zircons most likely were derived from a continent-absent, initially mafic to ultramafic protocrust that was multiply remelted between 4.4 and 4.0 Ga under wet conditions to produce more evolved (felsic) rocks. If the protocrust was produced by global mantle overturn at ca 4.4 Ga, then the transition to plate tectonics resulted from radioactive decay-driven mantle heating. Otherwise, such protocrust would have been the typical product of mantle convection and the transition to plate tectonics resulted from cooling and stabilization of lithospheric plates.

The influence of neutron irradiation and thermal annealing on helium diffusivity in apatite

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Accurate extrapolation of helium diffusivity over temperature and time is essential for quantifying long term erosion rates and the topographic evolution of Cenozoic orogens using (U-Th)/He thermochronometry. Naturally occurring radiation damage was recently shown to influence helium diffusion in apatite, such that the kinetics is controlled by the parent nuclide concentrations as an evolving function of time [1]. This implies that apatite helium ages are sensitive to lower temperatures and shallower depths than indicated by the diffusion kinetics presently observed in a given mineral. Here, we present results of controlled experiments to quantify the effects of (a) synthetic irradiation and (b) thermal annealing on helium diffusion kinetics in both synthetic and natural apatites. Exposure to a 1 MeV equivalent neutron fluence ($\Phi_{eq, 1MeV, Si}$) of 2×10^{18} n/cm² (90 hours in the cadmium lined in-core irradiation tube, CLICIT, facility of the Oregon State University TRIGA reactor) caused the helium closure temperatures (T_c ; 10 °C/My) to increase by up to +27 °C. The ΔT_c negatively correlates with the initial T_c , where apatites with higher initial T_c were less perturbed by the neutron irradiation than samples with lower initial T_c . Conversely, simply heating natural apatites to 550°C for 1 hour caused T_c in all cases to decrease to 47 ± 7 °C regardless of the initial T_c (the maximum observed $\Delta T_c = -44$ °C). The resulting T_c agrees well with diffusion parameters constrained [1] for radiation damage-free apatite, $T_c = 52$ °C.

These results clearly demonstrate that exposure to radiation causes the retentivity of helium in apatite to increase, whereas exposure to temperatures at which thermal annealing occurs causes the retentivity to decrease. The experiments suggest that after 1 hr at 550°C, effectively all natural radiation damage was annealed in each sample to yield a common T_c . This closure temperature (~47°C) would correspond to the diffusion kinetics in the damage-free apatite structure. From radiation damage theory we estimate the damage caused by the 90 hr neutron irradiation to be roughly equal to the alpha recoil damage corresponding to $[^4He] \sim 10^{-8}$ mol/g, or roughly the present 4He concentration of Durango apatite. This implies that Durango apatite should presently have $T_c \sim 27$ °C above the completely annealed state, or ~74°C, which is in excellent agreement with observations. This study highlights a need to quantify the kinetic effects of damage accumulation *and* annealing on helium diffusion in minerals used for (U-Th)/He thermochronometry.

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Geochemistry of Late Cretaceous tholeiitic volcanism and oceanic island arc affinities of the Chagai arc

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The major part of the Chagai arc occur in the western-north part of Pakistan and a small part of it also extends towards north in Afghanistan and west in Iran. The Late Cretaceous volcanic rocks which are designated as Sinjrani Volcanic Group, is the most wide spread and the oldest unite of the Chagai arc. This volcanic Group is mainly composed of basaltic to andesitic lava flow and volcanoclastics including agglomerate.

The petrological studies of various lava flow revealed that these are mainly basaltic-andesites (53.27-55.93 wt.% SiO₂) with minor basalts (49.57-52.14 wt.% SiO₂) and andesites (59.12-59.88 wt.% SiO₂). Petrochemical studies based on major and trace elements suggest that these are medium to low K tholeiites. The trace element show variable enrichment in LILE and depletion in HFSE relative to N-MORB. Their primordial mantle-normalized trace element patterns show marked negative Nb anomalies with positive spikes generally on K, Ba and Sr which strongly confirm their island arc signatures. The chondrite normalized REE patterns shows minor but variable enrichment of LREE and positive Eu anomalies. The Zr/Y versus Zr, and Cr versus Y studies, lowers Mg # and lower abundances of Ni and Co suggest that the parent magma of these rock suites was generated by about 15-30 % melting of depleted sub-arc mantle source, and fractionated in an upper level magma chamber en-route to eruption. These volcanics exhibit lower $^{87}Sr/^{86}Sr$ ratios (0.7038-0.7049), which are consistent with a depleted mantle source and closely correlate with oceanic island arcs rather than continental margin type arcs. On the basis of these studies it is concluded that the Chagai arc was initially developed as an oceanic island arc which was formed due to the intra-oceanic convergence in the Ceno-Tethys during the Late Cretaceous rather than constructed on the southern continental margin of Afghan block, as previously claimed by several workers.

The age of the Danube fault, 40 years after W. Schreyer

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As a result of his PhD study, Werner Schreyer published several papers about petrographic work in the Bavarian Forest where he investigated Variscan basement rocks close to the Danube valley. He also addressed the age of the Danube fault based on his observation from Natterberg, geological map sheet Deggendorf, and finally (in 1967) concluded that the Danube fault was formed during late-Variscan times and not, as suggested earlier (1961), during the Tertiary period.

The Danube fault stretches for about 200 km and is one of the most impressive fault lines in central Europe. As revealed by our recent field mapping, ancient motion along this fault has produced intensive cataclastic deformation along the Donaustauf segment of the fracture zone. The strain localised in this zone resulted in pervasive brittle deformation of the primary rock type, K-feldspar dominated granite. The cataclastic material was ultimately subjected to argillic alteration and K-feldspar was almost completely transferred into illite and other phyllosilicates. The crystallization age of the granite (known as "Kristallgranit") derived from an unaltered sample is 325 Ma (Pb- evaporation method) whereas the age of argillic alteration is constrained by K-Ar dating of illite fine-fractions (<2 µm) at 266 and 255 Ma. The new ages bracket the time of deformation and imply near surface exhumation of the fault rocks already during the Permian period, confirming Werner Schreyer's conclusion from 1967. Post-Cretaceous movement along the Danube fault, as indicated by offset of Mesozoic and Tertiary strata, did not re-open the K-Ar illite system. The illite ages also suggest that hydrothermal fluorite mineralization, genetically connected with the Danube fault, was an early Permian process.

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Peat deposits from Central Europe to the East European Plains investigated by uranium-series dating

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Interstadial and interglacial peat deposits are widespread in a transection between Central Europe, Lithuania, Russia, and Siberia, and enable us to reconstruct the vegetation history of the Northern Hemisphere. Multidisciplinary studies including lithostratigraphy, palaeontology, and palynology were performed by partners all over the transect. The reliable chronological frame for the reconstruction of climate and vegetation history was investigated by uranium series dating. The suitability of the peat layers for dating strongly depends on two essential prerequisites: (1) during the initial formation process any thorium was absent and (2) a geochemically closed system behaviour excluding uranium and thorium migration after deposition. However, peat may contain varying amount of admixed thorium by dust and clay minerals, while water passing through the peat layer can cause migration of uranium. Therefore, dating has to be carefully checked for the fulfilments of the prerequisites. Uranium series dating was performed on peat and organogenic deposits applying the thermal ionisation mass spectrometry (TIMS). Coeval peat samples were burned to ash and prepared by the leachate/leachate technique, spiked, and chemically separated for measurements of the isotopic composition. Once isotope activities are determined, age calculation depends on the evaluation techniques used to obtain reliable ages. The evaluation procedure includes (1) estimation of the thorium index by the isochron method to (2) correct the activity ratios for admixed detrital thorium, (3) calculation of corrected single ²³⁰Th/U ages, (4) checking corrected ages with the Chi-square test, and (5) calculation of weighted mean of isochron derived detritally corrected age for the deposit. The study of a variety of sections of burial peat on the transect gave a widespread overview on the suitability of peat deposits. Several case studies were investigated by uranium series dating. At the Netiesos section located in Lithuania, the age determination for the peat failed owing to the impossibility of determining an isochron to correct the single ages for the admixed detrital thorium. Furthermore, the investigation of the peat section of Gröbern, Germany, failed due to wide spreading activity ratios clearly demonstrating open system behaviour. Comparisons with radiometrically investigated uranium series ages retrieve the possible reasons. An isochron derived detritally corrected age of 219 ±8 ka was successfully determined for the peat layer from Krivosheino in Siberia, which is in excellent agreement with independent age control.

^{210}Pb - ^{226}Ra disequilibrium in basalts from Surtsey Island (Iceland) and implications for magma transport time

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Primitive basalts with radioactive disequilibrium between isotopes of the ^{238}U decay chain may provide constraints on the timescales of mantle melt migration. Few results still exist on the ^{210}Pb - ^{226}Ra disequilibria. Due to the short half-life of ^{210}Pb (22.3 years), only basalts significantly younger than 100 years old can be studied for ^{210}Pb - ^{226}Ra disequilibria generated in the magma plumbing system or the mantle. Most lavas measured so far show either ^{210}Pb - ^{226}Ra equilibria or ^{210}Pb -deficit which have been attributed to the degassing of ^{222}Rn in shallow magma chambers. Excess ^{210}Pb has also been observed in a few cases and explained by accumulation of ^{222}Rn that decays to ^{210}Pb . Icelandic tholeiites from the last century are in radioactive equilibrium with ($^{210}\text{Pb}/^{226}\text{Ra}$) equal to unity. These basalts are fed from shallow magma chambers having residence time exceeding 100 years. In contrast, primitive alkaline basalts (MgO = 7-12 %) from Surtsey island had ($^{210}\text{Pb}/^{226}\text{Ra}$) ranging from 0.45 ± 0.04 to 0.82 ± 0.06 at the time of eruption. These large ^{210}Pb deficits are unlikely to result from shallow magma degassing since no magma chamber existed beneath this volcanic island which was born during the 1963-67 eruption. The ^{210}Pb - ^{226}Ra disequilibria increase from the beginning towards the end of the eruption when the most primitive basalts were produced, and decrease systematically with increasing Th content. These same basalts show a negative correlation between Pb and Cu abundances which are inconsistent with exsolution of sulfur rich liquid or crystallisation of sulphides as a fractionation mechanism of ^{210}Pb and ^{226}Ra .

The large deficit of ^{210}Pb in Surtsey lavas were thus most likely generated during mantle partial melting. In such a case, the time of melt transport from the source region to surface is constrained to be significantly shorter than 100 years.

Climate changes and volcanic signals during the Bronze Age: A stalagmite record

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In this study we present high-resolution and multi-proxy records of a Holocene stalagmite showing *volcanic signals detected the first time in a stalagmite by REE analyses*. Stable oxygen and carbon isotope data profile along the speleothem deposited during the last 5000 years in the Mecsek Mts. (S-Hungary) suggest relatively stable conditions in most of the studied period. However, a significant $\delta 18\text{O}$ decrease ($>2\%$) between approx. 3800 and 3500 years BP occurs in the record. Fluid inclusion water shows also significant D-depletion, supporting cooling. Combined isotope and trace element measurements indicated coupled temperature and precipitation quantity changes occurring in the above period. Rare earth elements (REEs) were also measured by LA-ICP-MS technique, and unlike the longer trends shown by C and O isotopes, the REE and Y distributions indicate sudden changes at the beginning of the cooling period. The La/Y ratio of this segment shows similarities with the volcanic rocks of the Thera (Santorini) eruption that occurred at about 3650 years BP. As an independent indicator, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios show slight decrease at the REE peak, supporting the inferred volcanic signal.

The climatic conditions ameliorated rapidly (within ~100 years) to close to present day conditions as reflected by the C, O and H isotope compositions. However, some of the trace elements show marked changes following the recovery. Elements indicating detrital material within the carbonate matrix (e.g. Si, Al, Th) show marked elevations, along with $^{87}\text{Sr}/^{86}\text{Sr}$ increase, suggesting increased amount of silicious material transported by dripwaters. However, the Mg content is also higher at this section part, thus, the increase of detrital material amount may be related to lower carbonate precipitation rate, rather than to stronger weathering of silicate rocks.

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A geochemical gradient along the North Mid-Atlantic Ridge revisited: New Hf and Pb isotope data

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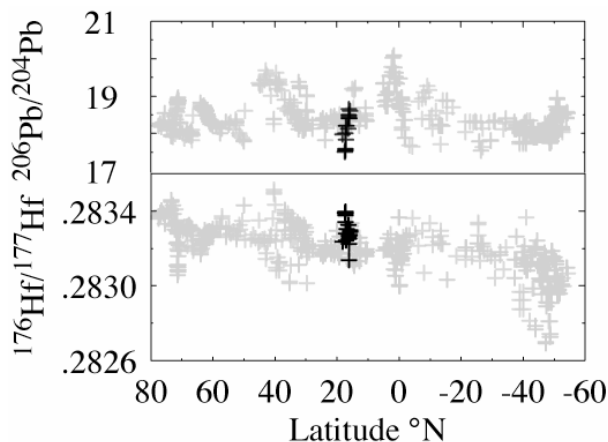
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Basalts dredged along the Mid-Atlantic Ridge north of the 15°20'N fracture zone and the so-called 14°N anomaly (Bougault *et al.*, 1988), from 15° 44' to 17° 28' show a well documented gradient from enriched to depleted chemical characteristics (Dosso *et al.* 1991) where Sr isotopic compositions vary from 0.70288 to 0.70217, respectively.

We will present new Hf and Pb isotope data for this region of the MAR. Preliminary results show that the Hf and the Pb isotope ratios range between the ambient local MORB mantle source that defines the 14°N bathymetric and C-like (Hanan and Graham, 1996) geochemical anomaly and an extremely depleted mantle source unlike any other so far recognized along the North Atlantic ridge. The results will be discussed in terms of the regional tectonic framework.



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Detection of biomarkers in oils using ToF-SIMS

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To identify biological traces in geological samples molecular biomarkers are widely used. Traditionally GC-MS (Gas chromatography-mass spectrometry) has been used for the analysis. In recent years when concentrations of target compounds were low surface sensitive ToF-SIMS (Time of Flight – Secondary Ion Mass Spectrometry) analysis has been applied. We present the results of a study using GC-MS and ToF-SIMS for the characterization of biomarkers in oils and oil extracts, aiming to prepare for the analysis of smallest quantities in oil samples recovered from fluid inclusions.

The biomarkers steranes and hopanes were characterized using polyatomic primary ion source (Bi_3^+) ToF-SIMS. These compounds were present in hexane extracts from natural oil samples by GC-MS analysis. The same extracts were analyzed by ToF-SIMS, allowing identification of individual biomarkers in this complex sample extract. This information was then used to interpret ToF-SIMS spectra derived from the crude oil by direct analysis. Although these spectra show the presence of a vast variety of components and compound fragments, the target biomarker components could be identified.

This initial study was done in preparation for the investigation of oil-bearing fluid inclusions in rocks from different environments and of different ages. Fluid inclusions may provide a wealth of yet undiscovered information due to their isolation from the environment. The capability to characterize smallest biomarker quantities from oil-bearing fluid inclusions contributes to the understanding of the environment in which the oil was formed and could provide insight into the biodiversity of early Earth.

Arsenic contamination of drinking water in some localities of Vila Real – Northern Portugal

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The occurrence of problems resulting from arsenic contamination of drinking water in Vila Real (Northern Portugal) was recognized by the Supplier Company of domestic water himself. One of the most significant water quality problems that will be present for a long time to come is the Rebordolongo site, which has arsenic contamination far in excess of any other area.

This preliminary study discusses the geological occurrence, the origin, the environmental impact and the health risks of arsenic in drinking water of the public water supply of Rebordolongo. The approach taken by this study was to compare the water quality were from boreholes and wells with the water quality in the homes of the consumers. Hydrochemical analyses have confirmed the presence of dissolved arsenic in drinking waters, with concentrations exceeding the current WHO potable water guideline. The total arsenic content of all these waters varies between <10 µg/L, and 28 µg/L.

The field work have confirmed placed near the one of the wells an abandoned wolfram mine, the waste from which is typically rich in arsenopyrite. The mineralogical composition of quartz-veins and waste samples from the mining site were undertaken to assess their potential as a subregional source of arsenic contamination. Tailings from the site are predominantly composed of quartz detritus with abundant arsenopyrite. The sulphides are mainly arsenopyrite and pyrite, with some galena and chalcopyrite.

The relatively high arsenic concentrations in the waters from the mine site may reflect the oxidation/weathering of arsenopyrite and other sulphide-bearing mine tailings. This allows for the solubilization of metals. Arsenic concentrations in domestic water were higher than those in the water from boreholes, probably suggesting direct mixing of effluent from mining area. Meanwhile, the domestic waters do not contain more than 14 µg As/L. However, arsenic is highly concentrated in the iron oxyhydroxides sampled in the bottom of the water reservoir. Upon contact with air, these waters locally form oxyhydroxides deposits, sorbing effectively arsenic. These deposits contain 0.83% As. Therefore, one can conclude that the environmental and health impact of these waters in Rebordolongo is not negligible.

A complementary phase that is in progress intends to characterise arsenic and heavy metals speciation more clearly and determine the link with iron oxyhydroxydes.

Global Ca-isotope signatures in post-Snowball Earth cap-carbonates

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$\delta^{44/40}\text{Ca}_{(\text{seawater})}$ values of Neoproterozoic cap-carbonates in NW Canada and NE Brazil overlying glacial units are reported. While cap-carbonates (Rapitian and Jaccoca Fms) overlying *ca* 0.74 Ga Rapitian diamictites display $\delta^{44/40}\text{Ca}_{(\text{seawater})}$ values increasing from -1.9‰ to -0.7‰, cap-carbonates (Raventhroat-Hayhook and Acaua Fms) overlying *ca* 0.635 Ga Marinoan diamictites display $\delta^{44/40}\text{Ca}_{(\text{seawater})}$ values decreasing from -0.9‰ to -1.8‰, followed by a progressive up-section increase to values near 0‰. The $\delta^{44/40}\text{Ca}_{(\text{seawater})}$ values displayed by the post-Marinoan cap-carbonates are undistinguishable from those of their correlative Kailber and Maiberg Fms (NW Namibia, Kasemann *et al.*, 2005). We suggest that changes in the $\delta^{44/40}\text{Ca}_{(\text{seawater})}$ values of the studied cap-carbonates reflect changes in the Ca-isotope composition of their coeval seawater. The similar $\delta^{44/40}\text{Ca}_{(\text{seawater})}$ values displayed by coeval carbonates from a deep to shallow marine profile (lower Hayhook Fm) suggest a homogeneous Ca-isotope composition of oceans. Differences in the degree of diagenetic overprint of these samples along with the sub-greenschists facies of metamorphism of the Brazilian cap carbonates suggest preservation of the sedimentary Ca-isotope compositions even after diagenesis and burial. The global nature of the $\delta^{44/40}\text{Ca}_{(\text{seawater})}$ values, along with varying Ca-isotope compositions with stratigraphy displayed by the post-Marinoan and Post-Rapitian cap-carbonate indicate that Ca-isotope stratigraphy can be used to correlate cap-carbonate successions worldwide.

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Macroscopic and infrared spectroscopic investigation of the synergistic effect between small organic ligands and desferrioxamine-B on the dissolution of goethite

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In several recent papers, Kraemer *et al.* [e.g. 1-2] have suggested that the dissolution of goethite by desferrioxamine-B (des-B) is enhanced in the presence of small organic ligands such as oxalate that actively shuttle iron from the goethite surface to bulk solution. The goal of the present study was to further an understanding of this phenomenon in both the oxalate- and malonate-goethite-des-B systems using macroscopic and spectroscopic methods. All experiments were performed at 25 °C in the absence of visible and ultraviolet light. The amount of oxalate and malonate adsorbed and the concentration of Fe(III) dissolved were studied after a reaction time of one week at total ligand concentrations between 0 and 5 $\mu\text{mol}/\text{m}^2$ and covering the pH range 3 to 9.5. Several different types of *in situ* infrared spectroscopic experiments were performed at constant pH values of both 4 and 6, total oxalate and malonate concentrations of 1 $\mu\text{mol}/\text{m}^2$, and des-B concentrations of between 0.1 $\mu\text{mol}/\text{m}^2$ and 1 $\mu\text{mol}/\text{m}^2$. First, spectra were collected to monitor the adsorption and surface speciation of oxalate and malonate on the goethite surface in the absence of des-B as a function of time, and the desorption of these ligands was followed spectroscopically to clarify the relative stabilities of the different types surface complexes. Second, spectra were collected as a function of time after the simultaneous addition of 1 $\mu\text{mol}/\text{m}^2$ concentrations of both oxalate or malonate and des-B to identify the complexes present at the goethite surface. Third, oxalate and malonate were reacted with goethite in the absence of des-B, and then spectra were collected as a function of time after repeated 0.1 $\mu\text{mol}/\text{m}^2$ additions of des-B every 24 hours. These experiments have revealed the type of surface complex responsible for the synergistic effect between these small organic ligands and des-B on the dissolution of goethite. The results are also discussed with respect to their broader implications toward mechanisms for ligand-promoted mineral dissolution.

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Variable Calcium isotopic fractionation factor in natural carbonated water

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Carbonates precipitated inorganically under laboratory conditions are fractionated relative to the coexisting solution by up to about -1‰ in their $^{44}\text{Ca}/^{42}\text{Ca}$ ratio [1,2]. Such Ca isotopic fractionation ($^{44/42}\alpha_{\text{carb}}$) is dependent upon the rate of carbonate precipitation with a temperature dependency as a knock-on effect [2] and has been attributed to kinetic effects. The mechanism by which Ca gets enriched in the light isotope in carbonate is rather controversial [1,2] but the experimental approach can be reconciled with the data obtained for biomineralisation. Evidence for a kinetic effect behind the preferential incorporation of light isotopes in inorganic carbonate is more elusive since studies at catchment scale [3-5] are complicated by the role of the vegetation and the incorporation or release of Ca by the biomass.

Here we report $\delta^{44/42}\text{Ca}$ for paired dripping water and speleothems previously studied for Mg isotopic fractionation [6]. The $^{44/42}\alpha_{\text{carb}}$ ranges from 0.9998 to 0.9988 while the $\delta^{44/42}\text{Ca}$ of the dripping water are either indistinguishable from the values of the country rock or enriched toward heavier values by up to 0.22‰. The largest $^{44/42}\alpha_{\text{carb}}$ is found in a slow dripping speleothem while fast dripping stalagmites precipitate carbonate weakly fractionated. Qualitatively, our data support Lemarchand *et al.* [2] model but with a much greater $^{44/42}\alpha_{\text{carb}}$ value for very low rate of carbonate precipitation. While this data is not direct evidence for an equilibrium fractionation of Ca isotopes, it is worth noticing that the incorporation of O and Mg isotopes in all of these speleothems occurs at equilibrium [6] and clearly suggests that the mechanisms responsible for Mg and O isotopic fractionations are distinct from those responsible for Ca isotopic fractionation.

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Lithospheric geodynamics with thermo-chemical density anomalies and mineral phase transitions switched on

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Density is an important physical property of rocks, which e.g. determines the isostatic response of the lithosphere to deformation. The density of a piece of mantle depends on pressure, temperature and composition. These three parameters inevitably change during geological processes such as rifting, but can also vary in apparently passive settings, e.g. at the lithosphere-asthenosphere boundary. The density distribution of the shallow mantle is non-linear and discontinuous due to complex mineralogy and, most importantly, phase transitions. The two shallow phase transitions that have the strongest effect on density are the plagioclase-in transition above ~50 km and the garnet-in reaction below ~40 – 100 km. The depth of these phase transitions strongly depends on the bulk composition of the mantle. The depth of the plagioclase-in boundary is mostly pressure dependent and predominantly controlled by bulk $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, whereas the garnet-in transition has a steep and curved Clapeyron slope with a strong depth-dependence on bulk $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$.

In an extending lithosphere, the density changes in the lithospheric column due to phase transitions can cause significant deviations from purely thermal subsidence. The amount of subsidence depends on the composition of the mantle, in addition to classical parameters such as the thickness of the crust, the initial geotherm and the amount of stretching. The phase-transition effect is most pronounced for thin crust, strong mantle thinning/upwelling and relatively fertile mantle compositions rich in aluminum and sodium, and can match the effect of thermal expansion. This could explain the pronounced syn-rift uplift and accelerated post-rift subsidence observed in some basins. The incompatible nature and strong mobility of sodium may lead to large changes in bulk Na_2O , and therefore density, during minor melting (Na extraction) or metasomatism (Na addition).

Densification of portions of the mantle, e.g., due to melt infiltration and shifts in the location of phase boundaries, might also contribute to the formation of gravitational instabilities and small scale convection, e.g. at the lithosphere-asthenosphere boundary. The combination of 2-D finite element deformation modeling and thermodynamic phase diagram calculations allows us to evaluate and quantify the feedback between geochemical variations and lithospheric deformation.

Elemental and Sr isotope investigations of human tooth enamel by laser ablation-(MC)-ICP-MS: Successes and pitfalls

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Sr isotope analysis of human tissue has proven to be an important tool for examining ancient human migration. Previous studies have typically conducted Sr isotope measurements by TIMS; however, Sr isotopic measurement by solution mode MC-ICP-MS greatly increases sample volume throughput with little (if any) detriment to the quality of individual analyses (e.g. Buzon *et al.*, in press). Recent studies have also reported reliable Sr isotope measurements and elemental concentrations within geologic and biologic samples at high spatial resolution using various LA-(MC)-ICP-MS instrument configurations. The relatively rapid nature of an individual laser ablation Sr isotope analysis (i.e. minutes) could possibly revolutionize (if successful) the manner in which migration studies of ancient civilizations are conducted in the future.

We investigated the elemental and Sr isotope ratios of tooth enamel from remains at the New Kingdom period Egyptian colonial site of Tombos (Sudan) by both laser ablation and solution mode-(MC)-ICP-MS analysis. Elemental abundances for both solution and laser ablation modes of analysis were obtained using a ELAN6000 quadrupole ICP-MS. Sr isotope measurements obtained in both solution and laser ablation modes were acquired with a NuPlasma MC-ICP-MS instrument. Laser ablation analyses were conducted using a UP213 system (New Wave Research).

Elemental abundances determined by both solution mode and laser ablation-ICP-MS analysis yield comparable values; however, $^{87}\text{Sr}/^{86}\text{Sr}$ values obtained by laser ablation are higher compared to their solution mode counterparts. This discrepancy is related to the production of a molecular interference- Ca+P+O (overlaps ^{87}Sr); hence the higher $^{87}\text{Sr}/^{86}\text{Sr}$ values recorded during ablation analyses. Laser ablation studies of enamel may provide relatively precise $^{87}\text{Sr}/^{86}\text{Sr}$ values rather quickly but cannot be used for accurately deciphering historical population migrations (Simonetti *et al.* in press).

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Characterizing degassing and magma recharge from measurement of short-lived U-series isotopes in volcanic gases and lavas

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Magma recharge and degassing are directly linked to volcanic activity. Determining the timescales of these shallow level processes is fundamental to our understanding of physical eruption dynamics and hazard assessment.

At many quiescent but potentially dangerous volcanoes, persistent degassing is the most common manifestation of volcanic activity. While it is generally agreed that these gas fluxes are mostly sustained by the exsolution of volatiles that were initially dissolved in the magma at depth, it has been unclear whether these gases originated from small ascending magma batches (ultimately recycled at depth once degassed) or large magma reservoirs beneath active volcanoes. Setting constraints on magma residence times in shallow degassing reservoirs and/or feeding systems is critical to distinguish between these two end-member models. Measurement of radioactive disequilibria between short-lived ²³⁸U-series isotopes in volcanic gases and rocks can provide previously unobtainable constraints on the timescales of shallow level magma dynamics (e.g. magma recharge and degassing).

We present new data on radioactive disequilibria (²²²Rn, ²¹⁰Pb, ²¹⁰Bi, and ²¹⁰Po) in gases and tephros collected from inside the Santiago Crater of volcano Masaya (Nicaragua). To our knowledge these are the first measurements of ²²²Rn from magmatic gases. Masaya's (²¹⁰Po/²¹⁰Pb) and (²²²Rn/²¹⁰Pb) are best explained by ²²²Rn enrichment and subsequent decay in gas bubbles of a magma body having a residence time between 3 and 150 years. Our measurements of radioactive disequilibria in Masaya's gases also display significant variability through time (periodically since 2000) that are correlated with observed variations in activity and gas fluxes at the surface. Taken together, these observations suggest that degassing occurs in a large magma reservoir beneath the active Santiago crater and that input of deep pristine magma into this reservoir controls the eruptive activity at the surface.

Anthropogenic signatures in sediments of the fast growing urban area of Natal (NE-Brazil) – A study of heavy metals and organic components

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In this study the effect of anthropogenic discharges on the composition of sediments in the Potengi – Jundiá river system near the fast growing city of Natal, NE-Brazil, is investigated.

In general, the sediments of the Rio Potengi – Jundiá river system in the studied area are not severely polluted. Rather they represent an incipient stage of anthropogenic accumulation. A previous study (Sindern *et al.* 2006) has shown that heavy metals such as Zn, Pb, Cu, Cd and in part also Sn, Hg and Ag have enhanced values relative to reference elements such as Al and Fe. Sources are domestic and animal waste, combustion products and hydrocarbons. These heavy metals are mainly bound to organic matter.

The elements Cr, Ni and V are characteristic of weathering heavy minerals in crystalline rocks exposed in the catchment area of the river system and are not significantly added from anthropogenic sources.

Additionally, a comprehensive spectrum of organic compounds was identified in sediment as well as water samples of the Potengi-Jundiá river system. Individual organic components were characterized dominantly to be of biogenic origin. However, huge amounts of indicative substances, e.g. fatty acids, suggest a significant emission of natural organic matter as the result of anthropogenic waste discharge. This might reflect incomplete of insufficiently working waste water treatment. Further on, well known xenobiotics, such as plastiziers, pharmaceuticals or pesticides, were detected only to a minor extend, although this type of anthropogenic contamination has frequently been found in riverine systems. The anthropogenic impact on the organic emission within the riverine system differs significantly from the organic signature of rivers from other regions, e.g. Europe or North America.

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Geochemistry and PGE potential of Bangur Gabbro from the Baula-Nuasahi Mafic Ultramafic Complex, Orissa (India)

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Geological set-up

The Baula-Nuasahi mafic ultramafic complex comprises of (1) Gabbro-Anorthosite unit, (2) Peridotite unit (with three chromite bands Ganga, Lakshmi and Sankar), (3) Pyroxenite unit and (4) Bangur Gabbro (~3.1 Ga) (Auge *et al.* 2003).

Geochemistry

The $Zr/TiO_2 \cdot 0.0001$ vs Nb/Y diagram shows these gabbros in the field of basalt. SiO_2 , Na_2O and Al_2O_3 shows negative trend while MnO and Fe_2O_3 show positive trend with MgO which indicates the differentiation trend of magma and is reflected in mineralogy. Trace element pattern of Bangur gabbro shows the positive Rb and Y anomaly and negative Nb anomaly. The positive anomaly of Rb and Y can be attributed to the development of secondary amphiboles due to alteration. The REE pattern suggests that these gabbros were derived from slightly enriched source.

The metal ratio diagram shows the PGE potential of Bangur Gabbro as almost all the samples plots in the field of Layered complex. So the samples plotted above the extrusive rocks field also show enough potential as the chrome-spinel in Bangur gabbro may have affected the ratio.

Discussion and Conclusion

The hydrothermal processes have lead to the formation of secondary minerals as well as remobilization of Base metal sulphide. The metal ratio diagram shows the potential for PGE and supports the further investigation to delineate the mineralized zone within Bangur gabbro.

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The Alteration Mineralogy and Mass Change of Volcanics from Zigana (Gümüşhane, NE-Turkey)

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The Late Cretaceous volcanic rocks around Zigana Mountain (Gümüşhane) at the eastern part of Black Sea Region (NE-Turkey) belong to the east Black Sea metallogenic province, and have intensive hydrothermal alteration although weathering alteration is limited. The basement of the study area is formed by the Late Cretaceous basalt, andesite and their pyroclastics. These rocks are overlaid by the Late Cretaceous aged dacitic rocks, namely Dacite-I and Dacite-II described by [1] and [2]. These volcanic rocks are bimodal in character and have tholeiitic to calc-alkaline affinity, and have developed in volcanic arc environment. The Late Cretaceous rocks are the host of VMS and vein type deposits in the study area and region.

Volcanic rocks in the study area have been altered to the sericite/illite-chlorite facieses, and contain sericite/illite, chlorite, quartz, carbonate minerals (ankerite and calcite), iron-oxide, and rare kaolinite, smectite and epidote as the alteration products. Sericitization/illitization is the most common type of the hydrothermal alteration associated with the Zigana Volcanics, and chloritization is the second. Pyritisation is seen all volcanics, and the most commonly in dacites. In some fields, limonitisation is occasionally present. Epidotization is rare, and especially seen at basalt and andesite. Isocon method was applied to estimate the mass gains and losses of the Zigana Volcanics as a result of hydrothermal alteration. According to this, basalt and andesite, Dacite-I, and Dacite-II have 2-61 % mass gain, 71 % mass gain and 42 % mass loss, and 44 % mass gain and 32 % mass loss, respectively. Namely, both mass gain and mass loss have occurred in volcanics during the hydrothermal alteration of the parent materials. Illitization-chloritization-kaolinitization increase generally from least altered rock to highly altered rock, whereas carbonatization decreases. The relation between metals such as Cu, Pb, Zn and sericitization/illitization, chloritization and silification shows that fluids which cause sericitization and chloritization did not increase the amount of these metals and, in fact, it can be said that these fluids are poor in these metals. This also shows that they developed under different hydrothermal conditions.

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Results of FTIR studying microdiamonds from gneisses and calc-silicate rocks from mine Kumdi-Kol, Northern Kazakhstan

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Statistically representative selection of microdiamonds from gneiss and calc-silicate rocks of the Kumdy-Kol deposit was first time studied by means of FTIR spectroscopy. Grayish yellow diamonds of the calc-silicate rocks are about 10-90 mkm in size and have cuboidal morphology. The morphology of microdiamonds from gneiss is more versatile. The crystals of octahedral, cubooctahedral and cuboidal morphologies were found there. They also have yellow color with grayish tint. The size of the gneiss microdiamonds varies between 15 and 150 mkm. The size of studied diamonds were about 60-150 mkm.

The selected diamonds have been studied with Bruker VERTEX-70 FTIR spectrometer equipped by Hyperion IR-microscope. IR spectra demonstrate that all of the studied diamonds contain nitrogen defects, which are manifested through the absorption at 1135 cm^{-1} (C-defects) and 1282 cm^{-1} (A-defects). Concentrations of nitrogen in the diamonds from different rocks are similar and vary from 700 to 2500 ppm ($\pm 20\%$). The nitrogen aggregation in the studied crystals varies from 30 up to 50% ($\pm 6-18\%$). The absorption at 3107 cm^{-1} indicates the presence of hydrogen defects. The intensity of absorption at 3107 cm^{-1} in gneiss diamonds is 5-20, while in calc-silicate rock diamonds - 2-10. Our data indicate that the studied microdiamonds belong to the Ib-IaA type.

IR spectra of diamonds from gneiss and calc-silicate rocks differ from each other in additional absorption lines. The spectra of calc-silicate rock diamonds testify to the presence of carbonate (1430 cm^{-1}) and silicate (1090 cm^{-1}) inclusions, water (banding vibrations at 1630 (1650) $\pm 5\text{ cm}^{-1}$ and stretching at 3420 cm^{-1}). The spectra of the gneiss diamonds do not demonstrate the presence of carbonates, silicates and/or water.

The differences of inclusion assemblages in microdiamonds from gneiss and calc-silicate rocks are the evidence of the extremely low mobility of the fluids/melts in the course of UHP metamorphism.

“Blood Coltan”: Fingerprinting of columbite-tantalite ores

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The term “Blood Coltan” was coined for columbite-tantalite ores in the Congolese civil war, as their sale supported the conflict, especially in the eastern provinces of the DRC. Following the United Nations initiative to fingerprint the origin of conflict materials, the German Ministry for Economic Cooperation and Development decided to fund this pilot study on fingerprinting coltan ores.

So far about 160 samples have been obtained from the world's major coltan producing areas. Special attention is directed toward the Ta-Nb-Sn provinces in Africa: DR Congo, Rwanda, Mozambique and Namibia.

Using state of the art analytical tools, we are investigating a wide range of mineralogical and chemical parameters obtained from columbite-tantalite ores, in an attempt to distinguish between different ore provinces, down to the individual deposit scale.

Methods employed include XRF (bulk major and trace elements), XRD (structure), ore microscopy, fully automated electron microscopy (Mineral Liberation Analysis), electron microprobe analysis (major and minor), laser ablation-ICP-MS (trace elements, isotopes), and TIMS (U-Pb dating).

Elevated concentrations of U, and low amounts of common Pb in columbite-tantalite, facilitate the application of the U-Pb system to date columbite-tantalite. Consistent results of TIMS and LA-ICP-MS analyses in three different laboratories prove that columbite-tantalite yields concordant and reliable ages. In the samples analyzed so far from Africa, four age populations are evident: Archaean ($>2.6\text{ Ga}$), Palaeoproterozoic ($1.9-2.1\text{ Ga}$), early Neoproterozoic (“Kibaran”; $0.98-0.93\text{ Ga}$), and early Palaeozoic (ca. 0.5 Ga). The bulk of the current Central African columbite-tantalite production is from Kibaran pegmatites associated with late “G4” tin granites. Trace element concentration patterns, mineral assemblages, and zoning characteristics in these pegmatites are clearly different from rare element pegmatite-hosted Ta mineralization in Alto Ligonha, Mozambique.

Study of trace elements reactivity in polluted soils: Measure of Cd, Zn, Cu and Pb lability by using DGT and isotopic dilution methods

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Industrial production and more precisely the metallurgy led to the dissemination of chemical contaminants in the environment. According to the metallurgical processes, this contamination can be more or less strong and induce, locally, grounds, water and plants pollutions.

In this study we try to quantify the labile pool of various trace elements in cultivated gardens, located around an industrial area.

The concentrations of heavy metals (As, Cu, Zn, Cd and Pb) measured in various cultivated vegetables are significantly higher than the european reference values (EC466/2001). The accumulation in plants differs in leaf, roots and fruits vegetables and is clearly correlated with the pH of the soils. In order to describe the heavy metal soil/plant exchanges, we tried to determine the concentrations of metals in the labile pool of the soils and to relate it to phytoavailability.

An isotopic dilution method (ID) using spiking with stable isotopes [1] and [2] has been performed in these polluted soils to determine the labile pool whereas a Diffusive Gradient in Thin film (DGT) method realised in the same soils permitted to mimic the heavy metal uptake by the roots of the plants [3]. The comparison between these two complementary methods allowed to describe the soil-solution transfer and demonstrated the different behaviours of the measured metals: relationships between labile pool measured by DGT and phytoaccumulation are observed for some of them, such as cadmium or zinc, but not for lead.

The kinetic aspects of the soil/solution exchanges were also described by performing ID and DGT, from 1h to 2 weeks. Modelization of these kinetics gave us the parameters describing the exchange properties and the desorption of the metal from soil to solution. These parameters varied with metal concentration, pH or organic carbon content in the soils.

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Organic microanalysis by time-of-flight secondary ion mass spectrometry

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Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is based on the analysis of positive or negative secondary ions emitted from a solid surface during bombardment by energetic ions. The technique has during the past decades become a well established surface analysis technique in materials science, in particular in the field of semiconductors and polymeric materials [1]. This is due to the attractive combination of high analytical sensitivity (in terms of absolute detection limits) and excellent imaging capability, with lateral resolution in the ~100 nm range. The application of the technique to more complex materials and molecular analysis was, however, for a long time hampered by the fact that the ionization process on which the technique is based lead to extensive fragmentation of and low yields (sensitivities) for organic analyte molecules of masses higher than a few 100 u. This was in turn due to the properties of the primary ions used for accomplishing the sputtering and ionization of the sample under study.

During the last few years, there has been a strong development around TOF-SIMS for the analysis of organic materials and molecules. In particular, the development of new cluster primary ion sources (e.g., Au₃⁺, Bi₃₋₇⁺, C₆₀⁺) have lead to dramatic improvements (typically by a factor 100-1000) in the detection sensitivity for organic molecules in the range from a few 100 u to 2000 u [2]. Due to the developments in instrumentation, in combination with a rapidly growing data base of reference spectra and the use of multivariate statistical tools for spectrum interpretation, TOF-SIMS is now emerging as a highly useful analytical tool for organic microanalysis, for example, in the field of biomedicine.

The presentation will give an introduction to TOF-SIMS, and illustrate the capabilities of the technique for analysis of organic materials. Opportunities for applications in the field of organic geochemistry will also be discussed.

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Fluid inclusions, REE and sulfur isotope geochemistry of the Lavrion carbonate hosted ore deposit, SE Attica, Greece

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The Pb-Ag-Zn sulfide mineralization of the ca. 3000 year old mining district of Lavrion, comprises mainly mantos and skarn-type massive sulfides. The area is a part of the Attico-Cycladic Belt (ACB). Late Miocene granitoid dykes and a granodiorite stock intruded the footwall of the detachment fault that separates the Basal Unit from the overlying Cycladic Blueschist Unit. Late Miocene porphyritic S-type granitoid rocks occur as sills along or within the hangingwall close to the detachment fault. The manto-type ores are spatially associated with the detachment fault, shear bands within marbles, and the shear contacts between marbles and the intercalated metaclastics of the Basal Unit, indicating that the most important structural control of the Lavrion mineralization is related to the large-scale back-arc Miocene extension in the Aegean. The mineralizing event postdated the mylonitic deformation stage of the marbles, as proved by the alignment of ore bodies with the mylonitic foliation planes or by their crosscut relationship. Wall-rock alteration is characterized by carbonatization and minor silicification. Ore deposition involved mainly marble dissolution and replacement, and open space filling.

Fluid inclusion studies provide evidence for deposition of sulfides of the manto-type mineralization at temperatures of about 280°C from fluids having salinities between 14 and 17wt% NaCl eq. Quartz and fluorite deposition occurred at lower temperatures (250 to 125 °C) from fluids having highly variable salinities (1-19 wt% NaCl eq.). The $\delta^{34}\text{S}_{\text{CDT}}$ values of galena, sphalerite and pyrite range between -4.8 to +3.99 per mil. Most paired samples of sphalerite-galena, sphalerite-pyrite and galena-pyrite show either reversed fractionations or unreasonably high temperature values, indicating either sulfur isotope disequilibrium or noncontemporaneous precipitation of sulfides. Chondrite-normalized REE patterns in fluorites show slightly increasing LREE and decreasing HREE contents. All fluorite samples possess weak negative Ce and pronounced positive Eu anomalies. A meteoric water influx late into the granodiorite stock is documented by the fluid inclusions in quartz of widespread extensional quartz veins. There is no clear evidence whether a direct genetic link exists between the manto-type massive sulfides and the Late Miocene igneous activity in the footwall of the detachment or along the detachment fault. Ag-rich sulfide mineralization forming tension gashes within hydrothermally altered hornfels postdates contact metamorphic phenomena.

Adsorption energy trends on UO₂ and ThO₂ surfaces

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Determining the interaction of adsorbates such as water and oxygen with surfaces of uranium and thorium dioxide is important for the long-term storage of these isostructural nuclear fuel materials. The semi-conducting versus insulating nature of UO₂ and ThO₂, respectively, makes comparison of surface-adsorbate interactions with these materials possible as a function of electronic structure in addition to surface structure. Previously, the quantum mechanical code CASTEP was used to calculate surface energies for UO₂ and ThO₂, and the (111) surface was found to be the most stable relative to the (110) and (100) surfaces in both cases (Skomurski *et al.*, 2006). In this study, CASTEP was used to investigate the interaction of water and oxygen with UO₂ and ThO₂ slabs of finite thickness representing each crystallographic orientation. The effect of model set-up on adsorption energy trends is discussed for single versus double-sided models in a periodic setting.

On a defect-free (111) surface, the adsorption of molecular water is found to be more favorable than dissociated water for both UO₂ and ThO₂. On the more reactive (110) surface, however, the opposite trend is favored. The adsorption of molecular and atomic oxygen is investigated as a function of spin configuration to determine the very first steps of oxidation on UO₂ surfaces. On both the (111) and (110) surfaces, the adsorption of atomic oxygen leads to oxidation of near-surface uranium atoms. Investigations into possible transition state spin configurations for oxygen interacting with the substrate are discussed. A co-adsorption case for water and oxygen is tested on both UO₂ and ThO₂ surfaces. On the UO₂ (111) surface, the presence of water is found to enhance the oxidation of near-surface uranium atoms, a phenomenon attributed to the semi-conducting nature of UO₂ as this trend is not observed on the insulating ThO₂ surface. Finally, the distance dependence of this "surface proximity effect" (Rosso and Becker, 2002) is tested as a function of distance between adsorbates on the (110) surface. By using quantum mechanical methods to investigate the very first interactions of oxygen and water with actinide oxide surfaces, we start to develop a mechanistic understanding of processes that ultimately affect oxidation and dissolution rates on the macroscopic scale.

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Garnet growth in the Zermatt-Saas Fee eclogites

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Different approaches have been used to infer the growth-limiting mechanism. The radius rate relations of e.g. Kretz (1973) rely on major element compositional zoning as time markers assuming that all porphyroblasts are precipitating the same chemical composition at any point in time. Comparison of chemical contour lines in variably sized garnets is used to distinguish between the different rate laws. A second approach is based on the 3-D spatial distribution of porphyroblasts. It assumes that depletion halos developing around early porphyroblast in the diffusion-controlled case will inhibit nucleation within the halos. This is supposed to lead to an ordered distribution while a random distribution is to expect for the interface-controlled case.

Application of the radius-rate concept to garnets of the eclogites of the Zermatt-Saas Fee ophiolite (ZSF, Western Alps, Switzerland/Italy) suggests that all garnets precipitated the same amount of radius per time interval, hence were grown limited by an interface-controlled growth mechanism. Approximately bell-shaped crystal size distributions suggest continuous nucleation and growth throughout the garnet growth history. Preliminary 3-D spatial distribution data using the nearest neighbour method point towards a random distribution, consistent with an overall interface-controlled growth mechanism, but tend towards an ordered distribution in rocks with higher modal abundance of garnet. This could be the case because new porphyroblasts cannot nucleate randomly if early crystallized garnets are abundant (e.g. Denison *et al.* 1997).

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Investigation of the interaction between green rust sodium sulfate and aqueous selenium

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Selenium is an important trace nutrient in the body at low concentrations but becomes toxic at high concentrations. It is a natural compound in many rocks and sediments in various concentrations, but selenium is also produced as a decay product in radioactive waste. It exists in various redox states of which the higher, selenate (VI) and selenite (IV) are mobile in the aquatic environment. Inorganic reduction to elemental, insoluble selenium is one pathway to minimize the bioavailability of selenium in areas of increased levels.

Green rust is an Fe(II)-containing compound, known for its capability of reducing a large number of oxidised elements and compounds. It belongs to the family of layered double hydroxides (LDHs) with layers of Fe(II)-Fe(III) hydroxide, separated by interlayers of water, anions and for some types also cations (*poster by Christiansen et al.*). The reduction of selenate and selenite by green rust has been studied during the last decade. We have focused our investigations at the nanoscale level to understand the mechanism of the reactions. We use transmission electron microscopy (TEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) to observe the particles at various times during the reactions.

Our results suggest that the mechanism of reaction is dependent on the type of green rust as well as the oxidation state of selenium. We used a green rust type which had SO_4^{2-} incorporated in the interlayers. When SeO_4^{2-} was added, we observed signs of intrusion into the interlayers. However, when SeO_3^{2-} , which has a different steric nature, was added, interlayer exchange was not observed. In both cases, the oxidised species were reduced to insoluble elemental selenium. Previous studies on chromate (Skovbjerg *et al.*, 2006) showed that the reduction mechanism is important for the mobility of the reduced contaminant, but in the case of selenium it appears not to be of relevance.

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REE distribution in volkhovites – New type of the tektite-like glasses

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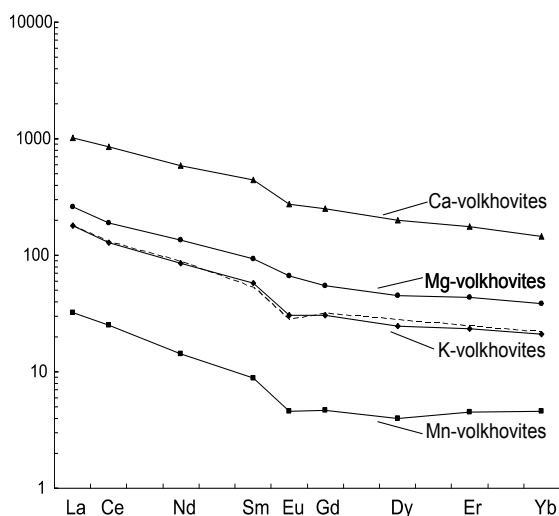
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Volkhovites are the tektite-like glasses of mafic and ultramafic composition; for the first time we have discovered them among fluvial-glacial sediments of Valday glaciations (10-65 thousand years) at the right side of the river Volkhov (North-West Russia). Volkhovite particles are characterized by small size (0.1-3.0 mm), varied microtektite aerodynamic (spherules, drop-shaped, dumbbell-like) and irregular forms, and the perfect safety indicating their postglacial age (Skublov *et al.*, 2007).

Volkhovites can be separated into four groups: Ca-enriched, Mg-enriched, Mn-enriched and K-enriched. REE distribution was studied in volkhovites locally by ion microprobe Cameca IMS-4f (IMI RAS, Jaroslavl, Russia). REE patterns for K-volkhovites and Australasian microtektites are very similar.

We suggest that volkhovites were formed as a result of outburst of the fluidite slag-stone-melt-mud-gas mixture from the crust deep levels up to surface (Skublov *et al.*, 2007).

Figure 1: Chondrite-normalized REE patterns for mean values for different types of volkhovites. Dotted line indicates the mean value for the normal Australasian microtektites (Glass *et al.*, 2004).



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Plešovice zircon – A new natural standard for U-Pb and Hf isotopic microanalysis

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Increasing number of geological applications requires the use of well-characterized and widely available reference materials for in situ analysis. We have established a new natural zircon standard ("Plešovice") for U-Pb dating and Hf isotopic analysis by laser ablation ICP-MS.

The ID-TIMS U-Pb age of the Plešovice zircon has been determined to 336.9±0.2 Ma (95% confidence limits; mean ²⁰⁶Pb/²³⁸U age). The U-Pb ages obtained by LA ICP-MS (3 labs) and SIMS techniques show larger spread but within their analytical uncertainties they are consistent with the TIMS age. Hafnium isotopic composition of the Plešovice zircon appears to be homogenous within and between grains. Combined laser ablation and solution MC ICP-MS analyses gave a mean ¹⁷⁶Hf/¹⁷⁷Hf value of 0.282481±0.000013 (95% confidence limits, 87 analyses). Cathodoluminescence and BSE imaging and chemical analyses revealed that discrete zones in the Plešovice zircon are enriched in trace elements and especially in U and Th. Raman spectroscopy suggests that these highly radiation-damaged areas have not undergone any annealing. Our LA ICP-MS analyses did not indicate any Pb-loss but the high intensities of measured U signal require that these areas are avoided during routine U-Pb isotopic analysis.

Constraining carbon sources and growth of microbialites in Pavilion Lake, BC using ^{14}C

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The morphologically varied freshwater carbonate microbialite structures in Pavilion Lake, B.C. Canada represent an opportunity to investigate the processes leading to their formation and potential associated biosignatures that will contribute to our understanding of geo-microbe interactions and to our ability to interpret the geologic record. A primary question in such systems is determination of the primary carbon sources and cycling. In some systems, such as Mono Lake, carbonate structures are proposed to be the result of abiotic precipitation due to supersaturation resulting from groundwater-surface water mixing. Alternatively, modern stromatolites such as those in Shark Bay and the Bahamas are proposed to form via significant biological influence using bulk DIC.

Determination of the $\Delta^{14}\text{C}$ of dissolved inorganic carbon (DIC) sources and mid-depth microbialite carbonate demonstrated that microbialite carbonate was significantly depleted in $\Delta^{14}\text{C}$ with respect to bulk surface water indicating either contributions of geologically derived carbon or significant time since precipitation. Assuming surface carbonate was recently precipitated, comparison to local and regional groundwater $\Delta^{14}\text{C}$ indicates that regional $\Delta^{14}\text{C}$ depleted groundwater DIC sources provide 12% of carbonate carbon.

$\Delta^{14}\text{C}$ of the detrital wood sample resulted in an estimated constant growth rate of 3 to 6 cm/thousand years, approximately double a previous U/Th based estimate.

The $\Delta^{14}\text{C}$ of a deep water carbonate sample was highly depleted indicating that either groundwater was making a larger contribution to this carbonate or that this carbonate was precipitated significantly earlier than the mid-depth carbonates.

Modeling marine Carbon and Phosphorus cycling during Cretaceous Oceanic Anoxic Events

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Phosphorus (P) is a key nutrient and may control rates of primary productivity and organic carbon (C) burial in the oceans. Changes in phosphorus (P) availability thus may have played an important role in the initiation, formation and termination of Cretaceous oceanic anoxic events (OAEs). Besides redox-dependent changes in the recycling efficiency of sediment P, as deduced from elevated organic C/total P ratios in black shales, the marine P cycle can be affected by variations in sealevel, oceanic circulation and chemical weathering.

In this study, we use a model for the coupled marine cycles of P and C to examine the relative role of these various factors in determining changes in P availability and organic C burial during OAEs. We focus on OAE-2 (~94 Myrs BP; 500 kyr duration) and specifically study (1) possible triggers for the OAE, such as enhanced weathering and reduced oceanic circulation, (2) factors leading to its termination and (3) the relative role of the continental shelves and open ocean.

Abiotic Nitrogen reduction in Hadean hydrothermal systems

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One of the outstanding questions in Astrobiology is the source and formation mechanisms of NH_4^+ which presumably was required for reactions of prebiotic synthesis and origin of life. The uncatalyzed reduction of abundant N_2 to NH_4^+ is prohibitively slow due to the strong triple bond in the molecule. However, NO_3^- and NO_2^- present in the Hadean Ocean as result of atmospheric reactions may have been more susceptible to reduction. We have experimentally tested the hypothesis, which suggests that Ni, Fe metals and alloys formed as a result of hydrothermal (HT) serpentinization processes in the Hadean oceanic crust could have acted as catalysts and/or reactants in reactions leading to abiotic NH_4^+ .

Our results show NO_3^- and NO_2^- were converted into NH_4^+ more rapidly than N_2 , and the reduction process had a strong temperature dependence. Metals, especially Ni were found to be more effective than alloys in reducing N_2 with yields usually not exceeding few percent. Based on the experimental results we have estimated NH_4^+ yield of Hadean HT systems from to be approximately 10^{10} - 10^{12} mol.yr⁻¹ which is comparable to values estimated by Brandes *et al.*, 1999 (10^{10} - 10^{11} mol.yr⁻¹) and Schoonen and Xu (2001) (10^8 - 10^9 mol.yr⁻¹) in HT systems as well as Summers and Chang (1993) for NO_2^- reduction by Fe^{2+} . Our estimate only includes N_2 to NH_4^+ reaction yield and therefore if $\text{NO}_2^-/\text{NO}_3^-$ were present in the advected seawater, the yields would have been proportionally higher considering their high conversion rates to NH_4^+ in the presence of metals/alloys.

We have also considered iron meteorites as possible sources of N since they commonly contain reduced N species such as nitride (N^{3-}) which could have reacted to form NH_4^+ during dissolution in the Hadean Ocean. When compared, however, with HT production, the meteoritic NH_4^+ flux during the Late Heavy Bombardment is approximately 6 orders of magnitude smaller.

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Melt segregation and near source fractionation: Examples from small scale basaltic systems

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Basaltic magmatic systems, expressed at the earth's surface as volcano fields, are characterised by very low rates of magma production ($< 1.0^{-4}$ km³ /year) over relatively long time scales (up to 10^7 years); these are tiny igneous provinces contrasting with Large Igneous Provinces that represent the other extreme in the spectrum of mantle derived magmatism. Tiny igneous provinces are the result of very small degrees of partial melting from a mantle source. In the Auckland volcanic field of Northern New Zealand, sampling of stratigraphically defined eruption sequences typically shows compositional trends in small magma batches that cannot be accounted for by fractionation involving low pressure mineral assemblages in a shallow pre-eruption environment. Detailed study of several individual volcanic centres in the Auckland field has defined two styles of compositional variation. 1). Least evolved compositions (as defined by geochemical parameters such as Mg-number and incompatible element content) are erupted first followed by more evolved compositions. This is interpreted to reflect magma extraction from a source in which a thermal gradient has produced a range of melting proportions with the greater proportion melt leading the extraction process. 2). The eruption sequence is initiated by relatively evolved compositions followed sequentially by progressively less evolved compositions. This trend is interpreted as the result of high pressure fractionation immediately above the source in a part of the conduit where melt is thermally connected to its surroundings and side wall crystallisation controls fractionation. The fact that these well defined compositional variations can be observed in stratigraphic sequence shows that the fractionated magma column rose very rapidly and without mixing once it left the source region. Further, such subtle compositional trends are probably only preserved because of the extremely small volumes of melt involved. In the Auckland volcanic field there is evidence for these extraction/fractionation processes occurring in both garnet and spinel peridotite facies giving rise to a range of alkaline to sub-alkaline basalt compositions. There is also evidence for compositionally distinct small magma batches coexisting independently and rising simultaneously to the surface demonstrating the inherent instability of small scale mantle based magmatic systems.

Purification of sterols and alkenones for compound specific hydrogen isotopic analysis using HPLC

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Here we present two variations of a method for purifying sterols and alkenones out of total lipid extracts using an HPLC-MS coupled to a fraction collector. The presented methods reduce the amount of work needed and simplify the procedure to obtain fractions pure enough for compound specific irm-GC/MS analysis, compared to traditional wet chemical techniques. This allows a higher throughput of samples so that high-resolution paleoclimatic or paleo-environmental proxy records based on compound-specific isotope measurements can be obtained more efficiently. The presented method was developed for hydrogen isotope analysis, and introduces no isotopic fractionation. The method could also be used in other cases where purification of lipid biomarkers out of total lipid extracts is required.

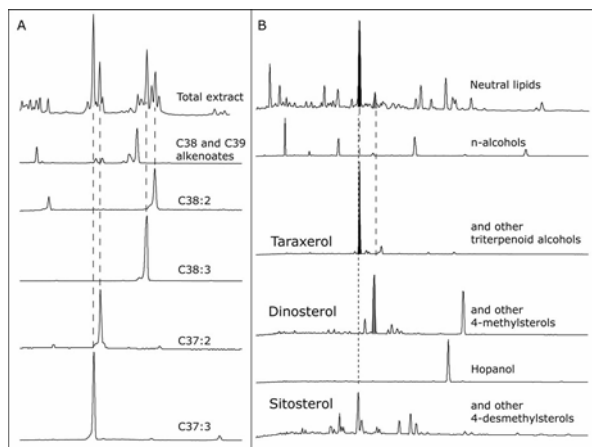


Figure 1: Gas Chromatograms of:

A) Total lipid extract of a Chesapeake Bay sediment and fractions as purified by semi-preparative HPLC. Individual alkenones are separated from notoriously co-eluting alkenoates.

B) Neutral fraction of a sediment from Palau (West Pacific) and collected fractions containing various alcohol classes.

Continental temperatures from the Paleocene-Eocene boundary in the Big Horn Basin, WY from carbonate clumped isotope thermometry

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We used carbonate clumped isotope thermometry to constrain growth temperatures of paleosol carbonates and fossil unionid bivalves collected from the Big Horn Basin (Wyoming) from sections that span the Paleocene-Eocene boundary. Long-term global warming of ~10°C occurred from the Late Paleocene to the Early Eocene. The Paleocene-Eocene Thermal Maximum (PETM) is an extreme thermal event of short duration (< 200 ky) superimposed on the long-term warming trend, and has been identified globally in the ocean sediment record and on the continents in sedimentary basins. The Big Horn Basin is one such basin that has been extensively studied with multiple climatic and biotic proxies in an attempt to characterize the PETM. Therefore, it is an ideal case study for the new paleothermometry technique we use here.

Temperature estimates for the paleosol carbonates capture the pattern of temperature change through time suggested by other paleotemperature proxies, but are consistently higher than previous estimates. Temperature estimates from the fossil mollusk shells, however, are too high to reflect original climatic conditions and do not mimic the stratigraphic change in temperature seen in other proxies. These samples were buried to > 1 km and subsequently exhumed. Our results suggest the paleosol carbonate samples were not dramatically reset by burial metamorphism, whereas the mollusk fossil carbonate was reset by re-crystallization or other processes. We speculate that carbonate that originally forms as calcite is more resistant to resetting during burial metamorphism than carbonate initially formed as metastable aragonite. Although X-ray diffraction analyses detected primary aragonite and no calcite in these fossil mollusks, trace metal analysis and more detailed SEM and/or XRD studies may be required to identify sufficiently unaltered fossil mollusks, if they exist (Came *et al.*, in revision, 2007). We conclude that the soil carbonate data constrain continental climate across the Paleocene to Eocene transition. In addition, the contrast between soil carbonates and fossil mollusks provides an important first case study of the relative ability of different forms of carbonate to retain primary temperatures as measured by clumped isotope thermometry.

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Melt inclusions and host olivines: What do they tell about mantle processes and sources?

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Host olivines and magmatic (melt and fluid) inclusion studies have had significant impact on petrology and geochemistry of mantle-related igneous processes in recent years. This includes better understanding of melting processes, source heterogeneities, and volatile contents of parental melts. At the same time, new results have shown possible processes (such as magma mixing and interaction with crustal materials) which appear to compromise the idea that melt inclusions represent simple primary liquids (e.g. Danyushevsky *et al.*, 2003). Here I present a summary of last 5 years studies of our group concerning compositions of melt inclusions and host olivines from the mantle plume, LIP and MOR environments.

Melt inclusions in olivines are likely trapped during relatively fast growth of crystals in the environments of significant temperature and (or) compositional gradients such as magma mixing. Compositional variability of melt inclusions far exceeds variability of lavas representing end-members commonly present in bulk rock in highly attenuated form. Melt inclusions of variable compositions coexisting in a single olivine phenocryst are often trapped sequentially at different depths. This suggests complicated multistage crystallization and trapping process rather than nearly simultaneous trapping of locally heterogeneous melts.

Data suggest that each volcanic plumbing system or particular lava represents dynamic mixing of numerous parental melts and products of their fractionation and (or) interaction with crystal meshes and melts in shallow conduits. Some inclusions approach primary melt compositions much better than any studied rocks. These inclusions show extreme compositional ranges far exceeding those of bulk surface lavas. They are usually trapped in the earliest crystals formed in the deepest parts of plumbing system. The compositional and isotopic ranges of the recovered parental melts suggest highly efficient open system melting; fast melt transport and compositional heterogeneity of mantle sources in all volcanic environments studied so far. In particular the concentrations of Mn, Ni, Ca, Zn and Sc of early olivine phenocrysts from wide range of mantle derived magmas are not consistent with common peridotitic source and suggest significant amount olivine-free hybrid pyroxenite source formed by melting and reaction of recycled crustal component in the convecting mantle (Sobolev *et al.*, 2005, 2007).

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Recycled oceanic crust as a source of Siberian flood basalts

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Recent study (Sobolev *et al.*, 2007) has shown that Gudchikhinskaya suit (Gd2) from the base of Siberian flood basalts in Norilsk region likely formed by melting of olivine-free hybrid pyroxenite, produced by reaction of melts from recycled crust and peridotite. Here we present new data on major and trace element compositions and volatile contents in parental melts for Gd2 basaltic suit recovered from the study of homogenised melt inclusions in olivine phenocrysts by EPMA, LA-ICP MS and SIMS. We show that the composition of trapped melt varies from similar to tholeiitic OIB (e.g. Mauna Loa, Hawaii) with notable depletion in Pb, U, Th and Rb to those enriched in these elements (Fig.1). Abundances of these elements correlate with concentrations of Si, K (positively) and Nb, Ti (negatively). This suggests significant contamination of melt by continental crust during magma fractionation. All melts are severely undersaturated by S and contain low water concentrations.

The composition of melts unaffected by crustal contamination indicate oceanic crustal component. This suggests that the recycled oceanic crust was a major source of Siberian flood basalts at the initial stage of LIP formation.

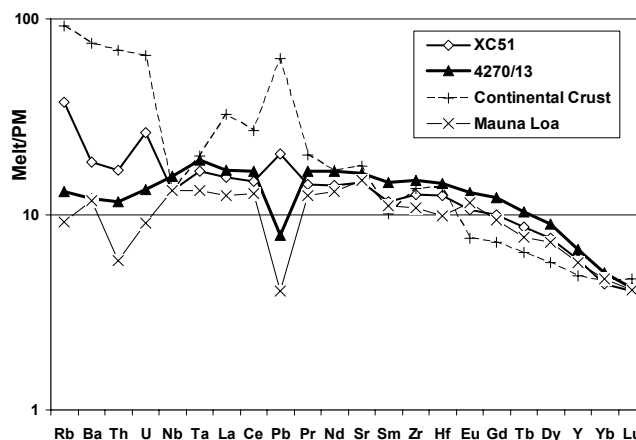


Figure 1. Average compositions of melt inclusions in olivine from Gd2 picrites (2 samples) compared with continental crust (Rudnik, 2003) and typical Mauna Loa melt (Sobolev *et al.*, 2005) normalized to primitive mantle (Hofmann, 1988).

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Evidence for correlation of late CFBs from East Greenland and the Faeroe Islands (North Atlantic Igneous Province)

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The Faeroe Islands formed early as part of the North Atlantic Igneous Province (NAIP) and is composed of a 4-5 km thick basaltic lava sequence erupted before and during continental breakup ~56-55 Ma ago (Storey *et al.* 2007). The present dataset represents the syn-breakup part of the sequence and comprises both enriched high-Ti plume related basalts and depleted MORB-like low-Ti basalts. The Faroese lavapile has earlier been correlated geochemically with the East Greenland Paleogene lavaseries from Kangerlussuaq and Blosseville Coast by Larsen *et al.* (1999), where the Faroes Middle and Upper Formations were correlated with the Milne Land Formation (MLF) from East Greenland. New data from the southern island of Sandoy on the Faeroe Islands shows that thin counterparts of the East Greenland Geikie Plateau Formation (GPF) and Rømer Fjord Formation (RFF) are present on the Faeroe Islands in the very top of the sequence. The correlation is based on variations in Zr/Nb and $^{206}\text{Pb}/^{204}\text{Pb}$ but is also consistent with petrological observations that GPF and RFF lavas are mainly aphyric and RFF lavas have lower contents of SiO_2 . This means that volcanism has proceeded longer than previously thought on the Faeroe Islands although in this area with much reduced eruption rates.

The isotopic compositions of the Faroes and East Greenland Palaeogene lavas show that the high-Ti basalts from MLF and GPF and their Faroese counterparts are all centered around the Icelandic IE2 end-member from Thirlwall *et al.* (2004), while the RFF lavas belong to the IE1 end-member. The depleted low-Ti lavas from the riftzone show only few examples of mixing between high and low-Ti magmas/sources and the low-Ti lavas can be modelled as mixtures between a MORB source and a component identical with the NAEM composition of Ellam and Stuart (2000). The proposed Icelandic depleted plume end-member ID1 (Thirlwall *et al.* 2004) does not seem to be present in the Paleogene lavas which is an argument against its existence.

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Occurrence and origin of igneous fragments in chondritic breccias

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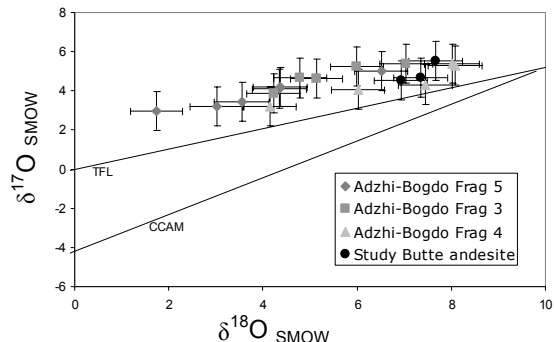
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The ordinary chondrite breccias Adzhi-Bogdo (LL3-6) and Study Butte (H3-6) contain igneous-textured inclusions that are best described as alkali-granitoids in Adzhi-Bogdo (Bischoff *et al.*, 1993) and andesite in Study Butte (Fredriksson *et al.*, 1989). Both the granitoids and the andesite appear to have been formed by melting and magmatic differentiation on a parent body and indicate mixing of achondritic fragments with chondritic components.

Al-Mg isotope data for these igneous-textured clasts reveal no evidence for radiogenic ^{26}Mg and indicate that the formation of these igneous clasts, the incorporation into the parent body regolith, and the lithification must have occurred late, after almost all ^{26}Al had decayed (Sokol *et al.*, 2007).

Oxygen isotope ratios of plagioclase, quartz and pyroxene in the fragments were measured in situ with the CRPG-CNRS Cameca IMS 1270 ion microprobe. On a three-O isotope diagram all fragments fall in the range of ordinary chondrites (Fig 1). These results imply that the fragments derive from an ordinary chondrite precursor and that the granitic fragments may have formed on the same parent body as the surrounding host rock material. The andesite seems to derive from a LL chondrite in contrast to its host rock (which is H3-6). This in turn indicates that melt formation and extreme differentiation occurred on ordinary chondrite parent bodies in the early stage of solar system formation. Alternatively, the fragments may have formed on another parent body but within the same oxygen isotope region of the solar nebula. In this case, they may represent projectile fragments within the chondritic breccias.



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New approaches to geochemical exploration for deep-seated and covered mineral deposits

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At present, because of the urgent need to carry out exploration for deep-seated mineral deposits, as well as deposits within areas covered by drifts, it is necessary to create and develop new geochemical techniques which are deep-penetrating ones and enable revelation of such concealed ore deposits. Routine geochemical prospecting surveys are not effective enough in such terrains due to low contrast or absence of geochemical anomalies related to ores.

Among the deep-penetrating geochemical methods based on the phenomenon of jet-flow vertical migration of chemical elements from the deep to the surface resulting in superimposed dispersion halos formation, is the Method of Analysis of Superfine Fraction (MASF) developed in VSEGEI that uses extraction and analysis of superfine fraction of soils (<3-10 μm) where superimposed dispersion halos occur. These halos are predominately created by the process of secondary fixation of mobile forms of elements due to the sorption of metals from the gaseous and water upward flows by clays, Fe and Mn hydroxides, and other natural substances. MASF surveys use sampling of definite horizons of soils and/or stream sediments, extraction of superfine fraction from samples by means of special technology, determination of contents of indicator elements using ICP-AES, ICP-MS, AAA with specific sample preparation, and geochemical data processing and interpretation with the help of original algorithms.

Another perspective technique is the geochemical prospecting using water-extractable and weak-acid-extractable forms of chemical elements (mobile ions) from soils and stream sediments. Results of our survey carried out in the Far East region has shown that most reliable prediction of gold mineralization can be distinguished by getting together data obtained by both mentioned deep-penetrating geochemical techniques.

Nisa granitic massif: SHRIMP zircon U-Pb age and source constraints

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The Nisa granitic massif crops out over an area of 1000 km² in SW Iberia. It is a zoned batholith dominated by a rim consisting of very coarse-grained porphyritic two mica S-type monzogranite-syenogranite and a discontinuous core of very fine-grained I-type tonalite-granodiorite. To constrain the age relationships and petrologic processes responsible for this zonation, SHRIMP ²⁰⁶Pb/²³⁸U zircon ages were obtained for the monzogranite and tonalite. Zircons from the monzogranite are typical of granitic rocks and can be broadly classified into three texturally and chemically distinct types: 1) high-U, low Th/U outermost overgrowths (307.4 ± 4.0 Ma); 2) moderate U and Th/U zircon with concentric zoning occurring both as inner overgrowths and whole grains (305.4 ± 6.2 Ma) and 3) texturally discordant cores (309.0 ± 4.6 Ma and inherited). It was impossible to identify in advance, on any textural basis, which cores were 'young' or inherited. Despite textural and compositional contrasts the three "young" zircon types have mutually indistinguishable ages. Zircons 1) and 2) represent different stages of igneous zircon growth and zircon 3) must represent an earlier stage of growth. Either the protolith of the monzogranite contained some zircon slightly older than the monzogranite itself or zircon grew in two stages, separated by a period of zircon undersaturation. The former hypothesis seems to be unrealistic in the regional geological context. The latter would be possible if the magma was reheated soon after cooling to the point of zircon saturation. This is consistent with the dissolution features found in some of both older and younger cores. There is a very marked chemical contrast between zircons 1) and 2), as Th/U in 1) is almost 10x lower than in 2), which is compatible with saturation of monazite at a late stage of crystallization and/or the presence of U-rich fluid soon after the monzogranite was intruded. The inherited old cores fall broadly into Neoproterozoic, near concordant ages (506–661 Ma), and Paleoproterozoic and older, mostly discordant ages (1.85–2.55 Ga). There is a noticeable absence of Mesoproterozoic ages, which is significant in a regional geodynamic context. In contrast, zircons from the tonalite have banded zoning that is typical of zircon from mafic igneous rocks, and inherited cores were not found. Further, their Th/U is generally >1, higher than in zircon from the monzogranite. Their age, 306.2 ± 3.0 Ma, overlaps the ages of the three generations of zircon from the monzogranite, but zircon features suggest different sources for these two granitoids. The tonalite protolith might have been a more refractory level that melted soon after the crystallization of the "young" zircon cores from the monzogranite due to an increase in temperature (causing zircon dissolution). Tonalite in the core of the batholith probably intruded immediately after the dominant monzogranite rim.

Land ocean interactions in a coastal embayment, Kaneohe Bay, Hawaii: Nutrient dynamics, productivity, and CO₂ exchange between seawater and atmosphere

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Human activities throughout the past two centuries have generated large increases in the atmospheric content of greenhouse gases, leading to higher global mean surface temperatures. The warming of oceans may increase the frequency of storms, which facilitate the transfer of nutrients, sediment, and pollutants from rivers into coastal ecosystems. Increased oceanic CO₂ concentrations attributable to anthropogenic input lower the saturation state of seawater with respect to carbonate minerals, can cause “ocean acidification” and have been argued by some to negatively impact calcification (e.g., Kleypas, 1999; Orr, 2005). Coastal areas and estuaries, however, may be either net annual sources or sinks of atmospheric CO₂ (-41 to 7.3 Mole C m⁻² yr⁻¹, Mackenzie and Lerman, 2006).

We present here results from 18 months of observations at CRIMP-CO₂, a collaborative effort in Kaneohe Bay, Hawaii between UH Manoa and NOAA/PMEL. This buoy was the first coastal buoy of the NOAA/PMEL-CO₂ program. CRIMP-CO₂ has documented the response of bay waters to pulsed inputs throughout a La Niña winter season (2005-06) and the much drier winter of 2006-07. The evolution of bay waters following storm-derived inputs was studied, along with the impacts of blooms and physical forcing on the air-sea exchange of CO₂. Physical forcing strongly influences system response, in particular stratification and mixing, hence controls both the duration of blooms and attendant changes in CO₂ concentration. Southern Kaneohe Bay often becomes a CO₂ sink following storm inputs (0.2-0.7 m Mole C m⁻² hr⁻¹), but remained a net source of CO₂ to the atmosphere (-1.06 Mole C m⁻² yr⁻¹) throughout our study period. This result is similar to estimates from Hog Reef flat in Bermuda and from the Scheldt Estuary plume (-1.2 and -1.1 to -1.9 Mole C m⁻² yr⁻¹, respectively, Mackenzie and Lerman, 2006).

Diamonds, xenoliths and kimberlites: A window into the Earth's Mantle.

UNESCO IGCP 557

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The principal aim of this study is to develop a dynamic process based understanding for the formation of the e- and p-type diamonds. A joint study of the petrology and geodynamics of diamond bearing rocks is thus understood as a space-time window for unravelling deep processes in the Earth's Upper Mantle. Our assessment aims particularly at the migration paths of hydrogen in nominally OH-free minerals in xenoliths, their geological/geodynamic setting as well as their petrological evolution. Recently, a 3-D dimensional modelling tool for understanding the geometry of a subduction zones was developed (Morra, *et al.*, 2006). The new method comprises a novel Finite-Element/Boundary Element method (FEM/BEM) coupled to a thermodynamic solver (PERPLEX). The primary target of the code was to give a quantitative tool for modelling mantle tomography and geodynamics using the constraint of phase equilibria. Although the simulations are mainly geared at subduction/collision environments, both methods can be used in a much broader sense and thus provide a unique opportunity to test geodynamic settings for diamond formation in a truly quantitative manner. The strength of the FEM-BEM method of Morra and Regenauer-Lieb (2006), lies in the fact that the physical parameters derived from thermodynamic calculations provide a robust tool for predicting a geodynamic processes. In our approach, density contrasts and mineral chemical compositions are used for driving geodynamic processes occurring in a subduction zone. Material parameters, are equally derived and complemented by the best of our knowledge on rheological properties of rocks from laboratory data. We propose to compare the predicted phases with *in situ* observations using multi-scale laboratory analyses complemented by a high resolution synchrotron based FT-IR analysis to derive passage of aqueous fluids through the lithosphere. This latter technique has proven to be very powerful to map the formation of mineral inclusions in mantle minerals such olivine. The project is carried out under the auspices of an international UNESCO IGCP557 collaboration involving a large group of international scientists.

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High sea bed methane emission rates at Hikurangi margin (New Zealand) associated with extremely dense populations of ampharetid polychaetes

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Occurrence of gas hydrates and gas seepage from Hikurangi margin sediments has been inferred from BSR structures, methane derived carbonates, gas flares in the water column, and the presence of chemosynthetic bivalve mollusks. Apart from these geophysical indications and sporadic observations by fishermen and scientific dredge samples, detailed biogeochemical studies are missing. We determined the in situ sea bed methane emission and associated fluxes of oxygen, nitrate, sulfate and sulfide at 3 different locations along the Hikurangi margin in water depths ranging from 662 to 1104 m using GEOMAR lander technology. Highest sea bed methane emissions of up to 203 mmol m⁻² d⁻¹ were associated with extremely high abundances of ampharetid polychaetes (10320 ind. m⁻²), highly elevated total oxygen uptake rates (up to 98 mmol m⁻² d⁻¹) and steep pore water gradients of methane, oxygen, sulfate and sulfide. Although members of the family Ampharetidae have been also reported from other cold seep sites and whale falls, this is to the best of our knowledge the first record where these polychaetes constitute key organisms of a cold seep environment. The distribution of the ampharetids was restricted to spatially highly confined patches of darkened sediment at the fringe of extended carbonate concretions. Close to these sites expulsion of free gas from the sea bed has been observed. They live in tubes of organic material that penetrate about 3 cm deep into the sediment. Density and spatial arrangement of their tubes, that extend a few millimeters into the water column, likely affects the current regime of the bottom contact water and therewith physical sediment properties and in consequence the exchange of solutes across the sediment-water interface. Micro gradients of oxygen and sulfide indicate further solute transport along the tubes. Both mechanisms might largely affect methane carbon turnover and release from this particular environment.

Sequential oxidation of arsenite by both permanganate and the reaction byproduct

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Arsenic contamination of soil, surface- and groundwater is of serious concern over the world because of its toxicity and carcinogenicity. One of the most effective ways to remove As from water is to oxidize it to less mobile and less toxic As(V), which can be subsequently immobilized by sorption to various sorbents. This study investigates the effects of permanganate on the oxidation of As(III) at pH 4 and 8 at varying doses of As(III) (10 or 100 µM) and permanganate (1 – 170 µM) in 0.01 M NaNO₃. The solution pH was adjusted to the desired values using 10 mM of either monobasic or dibasic phosphate buffer with 10 mM HNO₃.

The oxidation of As(III) by permanganate at the stoichiometric ratio of As(III) to Mn(VII) (i.e., 3:2 for As(III) oxidation to As(V) with an assumption of Mn(VII) reduction to Mn(IV)-oxide) or at excessive Mn(VII) concentrations is instantaneous at both pH's. In addition, the ratio of oxidized As(III) to reduced Mn(VII) is ca. 2.1, indicating the reaction product is probably Mn(III)-oxide/oxyhydroxide. When As(III) dose exceeds Mn(VII) concentration at pH 8, the excess As(III) is further oxidized by the primary reaction product, which is thereby reduced to dissolved Mn(II). This subsequent heterogeneous reaction between the excess of As(III) and the manganese solid byproduct is slower than the primary reaction. These results indicate that permanganate may be an effective and efficient reagent for As(III) oxidation in water treatment processes.

Study on 3-D crustal structure in the area along Yangtze River: The significance to multi-metal mineralization

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Introduction

The complex structure characteristics of the area along the Yangtze River in Anhui Province is located in the convergent collision belt formed by two big tectonic plates, which are North China Plate and Yangtze plate. Plenty of mineral sources were generated in the duration of the frequent magmatic activities in this area. Therefore, it has a significant meaning in the exploring mineral sources to get a comprehensive view of the 3-D crustal structure. Based on the inversion and integrated interpretation of six geophysical profiles across this area, we obtain the 3-D characteristics about the crustal structure in Anhui Province along Yangtze River.

Data Processing and Results

Taking the crustal structure of Yangtze Plate as the frame, and combining with the geological strata or tectonic units, the initial model containing the different blocks was designed. Taking the existing partially seismic profile interpretation as the constraint condition, gravity and magnetic robust iterative inversion and the 3-D crustal structure integrated interpretation are carried out in the six geophysical profiles across the entire area. Several conclusions were obtained as follows: (1) The crustal structure has the obvious three layers overall, namely the upper crust, the mid-crust and the lower crust. (2) The upper crust, with a violent changing structure, has deposited the relative thicker cap rock. The partial area may hit 10km, with the character of the low velocity, low resistivity, low density and low magnetism (V : 5.7~5.8km/s, ρ_s : 5~10 Ω m, σ : 2.6 $\times 10^3$ kg/m³, J : 10⁻²~10⁻¹ A/m). (3) The mid crust has the top depth generally below 10 km and the bottom depth generally about 20km, with the characteristics of high velocity, high resistivity, high density and high magnetism (V : 6.0~7.0 km/s, ρ_s : 1000~1500 Ω m, σ : 2.9~3.0 $\times 10^3$ kg/m³, J : n \times A/m), differently from the upper crust. (4) The lower crust, with an average of 12km depth, has the character of high velocity, high resistivity and high density (V : 6.8~7.6km/s, ρ_s : 10³~10⁴ Ω m, σ : 3.0~3.2 kg/m³). The Curie surface is in this layer. This study has significance to multi-metal mineralization.

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Historical variations in zinc stable isotope compositions of smelter polluted sediments

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Two case studies were carried out to investigate the use of zinc stable isotopes as tracers for industrial smelter sources and processes: 1) two organic sediment cores obtained 800 m from the former pyrometallurgical zinc smelter of Lommel (Belgium), which received exclusively atmospheric inputs, and 2) two dam lake sediment cores taken 15km upstream and 30km downstream of the former pyro/hydro-metallurgical zinc plant of Viviez (France), which received predominantly riverine dissolved Zn and particulate Zn inputs. Zinc isotopic compositions were measured on the LMTG Thermo-Finnigan Neptune MC-ICPMS in Toulouse and expressed as per mille deviations from the JMC 3-0749L standard. In case 1 atmospheric pre-industrial deposits have $\delta^{66}\text{Zn} = +0.31 \pm 0.09$ ‰ (2sd). Deposits dated from 1900-1930 have $\delta^{66}\text{Zn} = +0.29 \pm 0.06$ ‰ (2sd), and sediments dated from 1956-1995 shift to lighter isotopic compositions of $\delta^{66}\text{Zn} = +0.13 \pm 0.08$ ‰ (2sd) in 1968. 42 ZnS minerals from ore import dominating Australian and African mines yield, together with literature ZnS data, a grand average of $\delta^{66}\text{Zn} = +0.16 \pm 0.07$ ‰ 2se, n=83 for ZnS. Emission control since 1955 is a likely cause for the $\delta^{66}\text{Zn}$ sediment shift. In case 2 the polluted riverine sediments dated from 1952-2002 have elevated $\delta^{66}\text{Zn}$ of +0.75 to +1.32 ‰ relative to the geochemical background $\delta^{66}\text{Zn} = 0.33 \pm 0.06$ ‰ (2sd). Mine tailing slag samples also had elevated $\delta^{66}\text{Zn}$ ranging from +0.18 to +1.49 ‰. In summary we show that 1. Bulk ZnS ore minerals have homogeneous $\delta^{66}\text{Zn}$. 2. Zinc refinery processes fractionate Zn isotopes: slags are enriched in heavy isotopes. 3. near-field (<1km) atmospheric deposition resembles ZnS ores, far-field carries isotopically light Zn, and mine tailing drainage carries heavy Zn.

Diffusion profiles of Li in plagioclase/clinopyroxene and plagioclase/olivine intergrowths

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Diffusion in magmatic systems occurs during crystal growth, magma mixing and ascent. In some magmatic crystals diffusion profiles are preserved. These profiles provide information about the timescales of magmatic processes. It is known that Li diffuses very rapidly in plagioclase and clinopyroxene (Giletti and Shanahan 1997, Coogan *et al.* 2005, Parkinson *et al.* 2007) and that Li diffuses in plagioclase two to three times faster than in clinopyroxene (Coogan *et al.* 2005)

This study is focused on the diffusion of Li between intergrown plagioclase/clinopyroxene and plagioclase/olivine. These intergrowths are observed in andesitic and dacitic rocks from the volcanic island Nisyros (Greece). Plagioclase phenocrysts in the andesitic lavas are cloudy zoned with slightly higher An content in the cores, while olivine and clinopyroxene phenocrysts are not zoned. In the dacitic lavas plagioclase phenocrysts have complexly zoned ('splotchy') cores and low An rims, while clinopyroxene phenocrysts show nearly no zoning. Both intergrowths of phenocrysts were analysed for Li concentration. Concentration profiles across the minerals were measured using a Cameca ims3f ionprobe with ~ 5 µm lateral resolution.

Li concentration in the dacitic sample jumps at the border of the intergrowth from 10 µg/g in the plagioclase to 44 µg/g in the clinopyroxene and then drops steadily over a distance of 100 µm to 5 µg/g in the clinopyroxene core. Similar patterns are observed for plagioclase/clinopyroxene pairs in other dacitic and andesitic samples. In intergrowths of plagioclase and olivine in andesitic samples, the same Li increase on the border of the crystals is found (7 µg/g in the plagioclase to 13 µg/g in the olivine rim and a slow decrease to 5 µg/g in the core). Preliminary Li isotope measurements reveal negative $\delta^{7\text{Li}}$ values (~ -26‰) in clinopyroxene rims to zero values in the core. Isotope and concentration profiles are estimated to be caused by diffusion at ~ 1000°C and on timescale of only hours.

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Jadeitite, lawsonite eclogite, and related rocks, Guatemala: Fluid-rock histories from a cold subduction zone

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Jadeitite (jadeite rock) occurs rarely in a few serpentinite bodies from worldwide subduction complexes. Geochemical and CL-textural data show that much jadeitite crystallizes directly from multiply sourced Na-, Al, and Si-bearing fluids. Both jadeitite and lawsonite eclogite occur together in a few serpentinite-matrix mélanges of Guatemala. Also a rare rock, lawsonite eclogite forms under wet, extreme P/T conditions.

Each rock type shows complex fluid-rock interactions. Relationships of jadeitite-forming fluids and host rocks are all but unknown—such contacts are rarely preserved. In the Sierra de las Minas, a 3 m-wide pit exposes such a contact, with jadeitite and serpentinite respectively altered to albitite and meta-ultramafic rocks. At the paleocontact, Zr, U, Hf, Pb, Ba, Sr, Y and Cs are greatly enriched in albitite relative to the other rocks. Enrichments coincide with the appearance of and/or increase in abundance and/or grain size of zircon, titanite, celsian and REE-rich epidote in albitite. All contain albitite inclusions—many appear poikiloblastic—suggesting nucleation/growth of “trace-element-rich grains in albitite.

Lawsonite eclogite records another fluid-rock system. For example, sample 2-14 (Jalapa dept.) is LREE-rich, with La 50× and Sm 30× Chondrite. It contains lawsonite grains as: 1) 50-100µm, subidiomorphic inclusions in cores of 3-5 mm garnet₁; 2) 200-400 µm, irregular grains in garnet₁ rims; 3) 100-300 µm idiomorphic matrix, partly consumed by amoeboid titanite; 4) 100-300 µm, idiomorphic matrix, with 100-200 µm garnet₂; and 5) 300-600 µm idiomorphic late veins. Each textural type shows distinct LREE abundances and fractionations, as well as Sr contents and zoning (all by LA-ICPMS). Mass balance suggests only lawsonite (1) reflects “protolith” LREE values. The others manifest LREE redistribution, or deposition of exotic REE.

These data show that Guatemalan serpentinite-matrix mélanges yield field examples of the mobility of “immobile” elements under low-T (300-450°C), high to very high-P (~8-~23 kbar) conditions, in chemically distinct fluids.

Improved in situ measurements of lead isotopes in silicate glasses by LA-MC-ICPMS using multiple ion counters

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A new technique that improves the spatial resolution and detection limits of the measurement of lead isotope ratios in silicate glasses with < 15 ppm total Pb by laser ablation-multicollector magnetic sector-inductively coupled plasma mass spectrometry (LA-MC-ICPMS) is presented. The method allows for the concurrent, static measurement of ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , along with ^{202}Hg and ^{235}U , in six Multi-Ion Counters (MICs) fitted on a Finnigan NEPTUNE MC-ICPMS. Use of a collector array consisting only of MICs eliminates the need for cross calibration between Faraday cups and ion counters, as employed in previous methods reporting ^{204}Pb values by LA-MC-ICPMS. Standard-sample-standard bracketing using BCR-2G as the calibrant is used to correct for instrumental mass bias. Accuracy and precision of the method was evaluated by replicate analyses of various MPI-DING reference glasses, with low Pb concentrations (1.38 to 11.6 ppm total Pb) and well-determined isotopic ratios. Typical spot sizes for in situ analyses ranged from 40-69 microns, providing better spatial resolution than previous LA-MC-ICPMS reporting ^{204}Pb . Ablations for all analyses were carried out using a 193 nm ArF GeoLas laser at a repetition rate of 10 Hz and a pulse energy of 5 J/cm². Mercury derived from argon gas is a chronic problem for ICPMS measurements of the minor ^{204}Pb isotope because of the isobaric interference by ^{204}Hg . Due to the high sensitivity of the MICs, the Hg-correction of the measured 204-mass was significant, especially for samples with < 5 ppm total Pb. Two different methods were used to correct for Hg on the 204-mass with the results agreeing within error for each method on all lead isotope ratios. Measured lead isotope ratios for the MPI-DING reference glasses T1G (11.6 ppm Pb) and ATHO (5.67 ppm Pb) agree within 0.10% and 0.16% respectively of the accepted values. For MPI-DING KL2G (2.07 ppm Pb) and ML3B (1.38 ppm Pb), measured Pb ratios involving ^{204}Pb agree within 1% of the accepted values with typical precisions of < 2.9 % RSD (2 sigma). Measured $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for KL2G and ML3B are within 0.40% of the accepted values and typical precisions are < 0.75% RSD (2 sigma). The results for KL2G and ML3B demonstrate improvement over previous LA-MC-ICP-MS data in terms of both detection limits and spatial resolution, while retaining similar levels of accuracy and precision. The new method provides the capability of making quantitative in situ lead isotope measurements on tiny objects of geologic interest such as mineral growth bands, melt inclusions, and accessory minerals, even where they are lead poor.

Mineral phase identification of coral skeletal microstructure

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Mineral phase identification of the coral skeletal microstructure is important for reconstructing the paleoclimate. Especially, *Porites sp.* is widely used a paleo-climatic proxy. To reconstructing the paleo-environment, those chemical compositions have been studied as coral thermometry. For example, Sr/Ca ratio in coral skeletons is sensitive to the paleo-environment variant so that Sr/Ca ratio has the possibility as the accuracy archive. However, there are one assumption is that trace elements in coral aragonite originate from solid solution. Greeger *et al.* (1997) reported that the as much as 40% of strontium (Sr) in coral aragonite existed as a strontianite which was not the solid solution by using X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). On the other hand, Finch *et al.* (2003a, 2003) and Allison *et al.* (2005) showed no evidence of the presence of strontianite or its intermediate state in coral aragonite. They attempted to seek out the strontianite in coral samples using EXAFS. However, XANES and EXAFS could not identify the mineral phase directly. In addition, few studies have referred to mineral phase in coral skeletons with micro scale. X-ray diffraction analysis (XRD) with synchrotron radiation plays a role in detecting the mineral phase identification of coral skeletal microstructure for their strong energy, which enables phase identification with small range of X-ray spots: X-ray spot sizes of this study are 15µm and 40µm.

We performed XRD analysis with synchrotron radiation for coral, *Porites sp.*, living/fossil microstructure. The experiment conducted with imaging plate (IP) on BL-18c at Photon factory, KEK (HIGH ENERGY ACCELERATOR RESEARCH ORGANIZATION), Tsukuba, Japan. A monochromatic incident X-ray beam with a wavelength of 0.616Å was used and was collimated to a diameter of 15µm or 40µm. The two-dimensional IP data were integrated and conducted to one dimensional intensity data.

The size of the centre of calcification (COC) is approximately 30µm in diameter in the samples of this study. That size corresponds to the X-ray spot sizes of this study in 15 or 40µm in diameter, so we got the different mineral structural information between the COC and fibres. All diffraction peaks of COC and fibres can be explained as aragonite, and no significant difference of cell parameters can be observed. This indicates that COC and fibres consist of aragonite: this study could not detect calcite phase.

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Survival times of anomalous melt inclusions; Constraints from REE diffusion in olivine and chromite

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It is widely assumed that incompatible element diffusion through olivine and chromite is very slow and hence melt inclusions (MI) hosted in these minerals do not experience diffusive re-equilibration with the external magma. However, at present there are no data on diffusion coefficients for most trace elements in olivine or chromite.

We have conducted experiments at one atmosphere to determine diffusion coefficients for REE in forsteritic olivine and chromite. Clean samples of olivine and chromite that contain well-characterized MI suites were annealed with REE-doped (Pr, Ho, Tb, Lu) synthetic melts for up to 25 days at 1300-1450°C and under controlled fO_2 . Diffusion profiles were measured across sections of the crystal/synthetic melt boundary by laser-ablation ICP-MS and by electron microprobe. Element concentrations were then fitted to the diffusion equation to obtain diffusion coefficients. Calculated diffusivities for REE are relatively fast ($D = 10^{-15} \text{ m}^2/\text{s}$ at 1300°C), whereas P and Al diffusion appears to be very slow ($D < 10^{-18} \text{ m}^2/\text{s}$ at 1300°C).

MI in the olivine and chromite crystals have distinct enrichments in the REE that were doped in the external melts. The systematic degree of enrichment of $\text{Lu} > \text{Ho} > \text{Tb} > \text{Pr}$ and correlation between degree of enrichment and MI size and/or experiment duration are all consistent with re-equilibration of these inclusions via lattice diffusion through the host crystal.

Applying our diffusion coefficients to the equations of Qin *et al.* [1], we calculate that the REE compositions of olivine- or chromite-hosted MI will completely re-equilibrate with external magma in years to decades. These timescales are consistent with the REE enrichment observed in the experimental MI, and are significantly shorter than the times estimated for magma extraction from the mantle or residence in the lower crust. Therefore, anomalous MI must be trapped in the upper crust shortly before eruption. Our results show that the assumption of chemical isolation of incompatible elements in olivine and chromite-hosted MI is not valid, and hence calls for re-evaluation of the popular interpretation that anomalous MI represent preserved samples of unmodified mantle melts.

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Biogeochemical insight on the origin of carbonaceous matter in metalliferous lowest Cambrian black shale, South China

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Early Cambrian black shale deposits in the Yangtze Platform in South China are, in places, strongly enriched in Ba (~470 Mt barite and witherite), Ni, Mo, V, Co, Cr, Au, U, As, Pb, Zn, Cu, Re, and PGE. Several models have been put forward for explaining the extreme metal enrichment of the ~0.50-0.52 Ga old black shale. These include enrichment by diagenetic fluids, hydrothermal exhalation, extraterrestrial impact, synsedimentary enrichment from seawater, and discharge of petroleum into the basin. This communication presents the first results of a molecular and isotopic organic geochemical study of the metalliferous carbonaceous shale. The new biogeochemical data provide further insight into the source of the hydrocarbons and the formation of the organic matter-metal association.

The TOC content of the analysed samples is between 0.7 and 8.2 wt%. The Rock-Eval parameters were not reliable in most samples because of the low S_1 and S_2 peaks. The massive aspect of the samples without altered surfaces and coating of metal oxyhydroxides suggest indigeneity of the organic extracts. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios of the kerogen range respectively from -31.5 to -35.4‰ V-PDB and from -1.4 to 0.6‰ V-Air. The $\delta^{34}\text{S}$ values of the organic-solvent soluble molecular sulphur of black shale samples range between 13.9 and 15.8‰ V-CDT, similar to the values obtained for sulphides.

The distribution of saturated HC are characterized by: *n*-alkanes in the C_{11} - C_{31} range (maximum at C_{16} , bimodal distribution with further maxima at C_{22} or C_{26} in some samples, slight even-over-odd dominance), moderate to large *i*- C_{18} to *i*- C_{21} isoprenoid peaks, pronounced unresolved naphthenic humps in the *n*- C_{15-22} range, generally pristane and phytane in roughly equal proportion, and alkylcyclohexanes in the range C_{11} - C_{28} . Some bitumens contain C_{27} - C_{35} hopanes and C_{27} - C_{29} steranes, with the latter dominating over the former. Aromatic HC such as alkylbenzenes, naphthalene, and alkylnaphthalenes were detected only in very minor concentrations. The $\delta^{13}\text{C}$ values of *n*-alkanes and isoprenoids vary between -33 and -25‰. In all samples pristane and phytane are depleted in ^{13}C by up to 6‰ compared to C_{17} and C_{18} *n*-alkanes. All these results are best explained by derivation of hydrocarbons from algal and bacterial mats that were deposited in a saline, anoxic marine environment.

Chlorine Partitioning: The behavior of Cl in the presence of sulfide - silicate melts and aqueous fluid

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Can sulfide melts exsolve halogen rich fluids? Several ore deposits around the world (eg. Broken Hill, Stillwater, Sudbury and Bushveld) have occurrences of halogen-rich minerals in association with the ore. To help better understand these occurrences, piston cylinder experiments were performed to investigate the partitioning behavior of Cl between coexisting haplogranite and Pb-Fe-Zn-sulfide melts at 0.5 GPa pressure and 810°C temperature.

In water undersaturated experiments where a Cl doped haplogranite glass was used as the silicate starting material, the Cl was found to partition strongly into the sulfide melt. Here Cl may be acting as a flux within the sulfide melt resulting in lowering its eutectic temperature. Not only is Cl dissolved in the sulfide melt, but as the sulfides crystallize the residual sulfide melt progressively enriches in Cl. In water saturated experiments where Cl was doped into the sulfides, Cl was noticeably absent from both quenched sulfide melt and silicate glass, suggesting strong partitioning into the coexisting aqueous fluid. The results indicate that the partitioning preference of Cl, when in equilibrium with sulfide-silicate melts and aqueous fluid, decreases in the order aqueous fluid - sulfide melt - silicate melt.

These experimental results can be applied to understand the cooling of sulphur- and chlorine-bearing magmatic systems. Initially, Cl will partition into a sulfide melt that coexists with a hydrous silicate melt. Once an aqueous fluid exsolves from the silicate melt – due to decompression or crystallization at the solidus – Cl will partition into the newly formed fluid causing the sulfides to freeze and crystallize rapidly. The escaping Cl-rich fluid might lead to extensive halogen alteration in the country rocks of the intrusion. The concepts investigated in this study may have significant implications for understanding the evolution of magmas giving rise to copper porphyry deposits and aid in our understanding of halogen-alteration and halogen-rich minerals in major sulfide deposits.

Planktonic foraminifera: Calcifying microenvironments, diffusive boundary layers and a peek at the event horizon

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The planktonic foraminifera, *Orbulina universa*, should be considered the proverbial white rat for researchers studying biomineralization in the marine realm. This protozoan produces a spherical test in a single brief (several hours) calcifying event, that involves organic matrix secretion, rapid calcite precipitation and spine elongation. Chamber thickening in subsequent days is intimately linked to diurnal physiological oscillations related to symbiont photosynthesis and host assemblage respiration which controls large shifts in microenvironment pH (7.8 – 8.8) and [O₂] (~80-220% air saturation) (Rink, *et al.*, 1998). Interestingly, microelectrode measurements of Ca²⁺ at the chamber surface show concentrations that are 10% higher than ambient seawater, while [CO₂] measurements on *O. universa* under dark and light conditions suggest ΣCO₂ varies between ambient (~2 mMol/kg) and ~5 mMol/kg respectively in the boundary layer near the calcifying shell (Köhler-Rink and Kühl, 2005). Together these data point to an active calcium and carbon concentrating mechanism in this species, and may help explain how *O. universa* can calcify in seawater at pH between 7.4 and 8.8 (Bijma, *et al.*, 1999).

Laboratory experiments and stable isotope and trace/minor elemental analyses of *O. universa* demonstrate that shell geochemistry is influenced by physiologically-controlled boundary layer chemistry. Elemental ratio banding, possibly related to the diurnal cycle, as well as observations of non-equilibrium calcite precipitation, provide insight into aspects of calcification that were previously poorly constrained. Together, these observations may provide clues for novel applications of foraminifera geochemistry for paleoenvironmental reconstructions.

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Trace elements in garnets of diamondiferous xenoliths from the Nurbinskaya pipe, Yakutia

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Rare earth elements (REE) and other trace elements were analyzed by LAM-ICPMS in garnets of about 150 mafic and ultramafic diamondiferous xenoliths from the Nurbinskaya pipe. Most garnets are homogeneous in terms of major- and trace-element contents. Garnets from ultramafic xenoliths define two groups, one with sinusoidal REE_N (chondrite normalised) patterns (10 harzburgites, two lherzolites) and one with flat MREE_N (lherzolites, some websterites).

Most eclogitic garnets have LREE-depleted patterns (Ce_N as low as 0.1), and no Eu anomalies. Heavy rare earth elements are variably enriched; most Lu_N varies 20-50. Most websteritic garnets show REE patterns similar to this but they are typically enriched in LREE with Ce_N (0.2-0.5). Garnets with nearly flat HREE and small positive Eu anomalies are common in coesite-bearing eclogites and those containing kyanite and/or corundum [1]. Another group of garnets (n=9) from eclogites and websterites have small negative Eu anomalies. These types of pattern commonly are interpreted as evidence of the reaction of plagioclase to garnet and used to support the origin of mantle eclogites by subduction of oceanic crust [1, 2], but may be simply a redox feature. Garnets from highly aluminous eclogites show convex REE patterns enrichment in LREE and strong depletion of in HREE (Yb_N<5). Garnets of corundum-bearing eclogites commonly have positive slopes within the LREE_N, peaking at Sm and then slowly decreasing to about chondritic abundance for Lu. LAM-ICPMS analysis could be used to show how different populations within an eclogite xenolith series can document the heterogeneous evolution of the lithospheric mantle beneath cratonic areas.

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Latest-stage exhumation history of the Central Alps

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The European Alps, like many other Cenozoic orogens, show a pronounced increase in erosion rates since ~5 Ma. In a recent paper, Willett *et al.* (2006) proposed that this accelerated erosion was due to enhanced precipitation subsequent to the Messinian salinity crisis and marked the transition from orogenic construction to orogenic destruction.

In this study, the latest-stage exhumation history of the Central Alps was investigated by using zircon fission track (ZFT), apatite fission track (AFT) and apatite (U-Th)/He (AHe) thermochronology along the eastern margin of the Lepontine Dome. The study area covers basement nappes east and west of the Forcola fault, a major Alpine normal fault bordering the Lepontine Dome to the east.

ZFT ages from both east and west of the Forcola fault range between 25 and 16 Ma, with youngest ages occurring close to the fault system. These ages reflect a period of enhanced exhumation related to the onset of orogen-parallel lateral extension of the Alps. The area east of the Forcola yielded AFT ages between 17 and 5 Ma and AHe ages between 7.5 and 6 Ma, whereas the area west of the Forcola yielded AFT ages between 9 and 4 Ma and AHe ages between 6.6 and 3.4 Ma. The age difference between basement nappes east and west of the Forcola normal fault indicates that the fault system has been active (or re-activated) during the Latest Miocene to Pliocene, much later than previously assumed. Late Neogene reactivation, however, has also been observed for the Simplon normal fault west of the Lepontine Dome, which is supposed to be conjugated to the Forcola fault. Age-elevation relationships reveal that the area west of the Forcola fault experienced a period of rapid exhumation between approximately 5.5 to 4 Ma, and that exhumation rates slowed down after ~4 Ma. The period of rapid exhumation is temporally consistent with the increase in deposition rates in the foreland basins, whereas the end of rapid exhumation coincided with the end of deformation in the Jura mountains. These temporal relations support the idea of a Pliocene shift from orogenic construction to orogenic destruction and thus to a decrease of the actively deforming area of the Alps.

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Spatial record of recent anthropogenic changes in the sedimentary soils of the Netherlands; Opportunities for a knowledge-based soil legislation framework

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Much of our knowledge about recent environmental changes – such as the increased anthropogenic emission of various metals – has been inferred from sedimentary records. These paleorecords, however, mainly focus on environmental changes through time. To generalize such changes in a spatial context, geochemical baseline surveys are required.

Using the data from the Geochemical Soil Survey of the Netherlands (Van der Veer, 2006), a geochemical baseline model was developed. The baseline model, based on covariability in pristine sediments, revealed a substantial overall enrichment of metals including Cd, Cu, Hg, Pb and Zn. These enrichments reflect the accumulation of metals in the topsoil compartment as a result of ongoing diffuse input from various anthropogenic sources. The enrichment, generally a factor 2-3 above natural concentrations, varies on a local as well as a regional scale.

Besides tracking environmental changes in a spatial context, the model furthermore offers unique possibilities to derive soil quality standards for a knowledge-based soil legislation framework. In this presentation we will show how the model can be used to derive soil quality standards, and how to take the natural variation of soils, as well as the diffuse enrichment, into account.

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Bionergetics of the buried seafloor

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Major questions in subsurface biosphere research are related to bioenergetics. How much energy is required to support a given amount of biomass? And what is the minimum energy yield of reactions that are biologically utilized? Beyond these, there are related issues, such as, the energetic rules that govern the distribution of subsurface life, in particular, the controls on the distribution and rates of the various energy producing metabolic reactions and the possibility that some buried marine ecosystems rely on radiolytic H₂ as their principle electron donor.

In situ metabolic rates and energy yields of diverse microbial activities in sediments of the eastern equatorial Pacific have been determined based on sedimentary pore fluid chemical profiles. Fe and SO₄⁻² reduction, and methanogenesis co-occur. These are energetically favorable throughout the sediment column with relatively constant energy yields. Based on this, minimum biologically utilizable energies of reaction can be inferred and it appears that this ecosystem operates as a thermodynamic homeostat.

When combined with reaction rate estimates, based on a numerical solution to the diffusion/reaction continuity equation, these data allow the calculation of an average maintenance energy that is orders of magnitude lower than observed in the laboratory. Based on this, it is inferred that in marine sediments, radiolytic H₂ could support approximately 10⁵ while approximately 10⁴ could be supported in a water-saturated sediment that has a U, Th, and K similar to that estimated for the Martian crust.

Plate-tectonic controls on intraplate volcanism in New Zealand

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Cretaceous to recent intraplate volcanism in the New Zealand microcontinent provides an ideal case to explore possible factors that exert control on this type of volcanism. Located in the vicinity of the active Australian-Pacific plate boundary, the New Zealand microcontinent exhibits intraplate volcanic activity that is associated with various tectonic regimes: behind an active arc, in domains with predominant strike-slip motion, and in areas that are virtually unaffected by recent plate-tectonic activity.

Based on major-, trace-element-, and Hf-Nd-Pb-Sr isotope compositions of a representative set of near-primitive samples, distinct end member compositions corresponding to different tectonic regimes can be recognized: (1) HIMU-like signatures ($^{206}\text{Pb}/^{204}\text{Pb}$ up to 20.57, “decoupled” Hf-Nd systematics; e.g., Chatham Islands), (2) dilute HIMU-like trace element signatures and depleted, asthenospheric isotope compositions ($\epsilon_{\text{Hf}}: +9.9$, $\epsilon_{\text{Nd}}: +7.0$; North Island), and (3) compositions having affinities to subducted sediments ($^{87}\text{Sr}/^{86}\text{Sr}: 0.7037$, $^{206}\text{Pb}/^{204}\text{Pb}: 18.99$, $^{207}\text{Pb}/^{204}\text{Pb}: 15.67$; South Island). The HIMU- and sediment-like signatures are interpreted to originate from a veined lithospheric mantle, reflecting a variable overprint by an ancient, possibly Cretaceous mantle plume and by Phanerozoic subduction zone enrichment.

Variations in the average melting depths of the magmas are manifested in a variable impact of residual garnet (e.g., $\text{Gd}_N/\text{Yb}_N: 1.84 - 4.74$). Changes in relative melting depths reflect variations in lithospheric thickness [1]. The geodynamic setting (lithospheric thickness, heat flow, degree of extension) controls the proportions of asthenospheric and lithospheric source components. For the South Island, magma compositions provide “snapshots” of a decreasing lithospheric thickness beneath active volcanic fields since ~20 Ma. This finding is in agreement with recent geophysical data that suggest the presence of thickened, dense lithospheric mantle beneath the Southern Alps (collision zone) but not beneath the intraplate volcanic fields east of the plate boundary [2]. It has been proposed that the regional thickening of the lithospheric mantle is a result of ongoing oblique convergence and strike-slip motion [e.g., 2]. We propose that the same processes also caused regional transtension and thinning of adjoining parts of the lithospheric mantle, thus controlling the composition of the intraplate volcanic rocks.

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The Podili alkaline complex, Prakasam alkaline province, Andhra Pradesh, southern India

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The Podili alkaline complex in Prakasam alkaline province of Andhra Pradesh, in the southern India, is one among the cluster of alkaline complexes with a near NE-SW disposition pervading the cratonic corridor that is terminated by intracratonic sedimentary Cuddapah Basin in the west and Eastern Ghat Mobile belt in the east.

This N-S trending complex (12 km²) has a close spatial and temporal association with granites and gabbros that represents the manifestations of basic, acidic and alkaline magmatism.

Alkali syenite, and subordinate quartz syenite constitute the important lithounits of the complex.

The syenites are leucocratic dominated by microcline mesoperthite, plagioclase feldspar, ±quartz. The mafic minerals are alkali pyroxenes and biotite with subordinate magnetite, sphene and apatite. The mafic minerals attribute to the alkaline and hydrous nature of parental liquids.

The syenites are of different degrees of silica saturation, and alkali syenites in particular carry normative nepheline and aegirine, an indication of the peralkaline trait possibly inherited from the parental alkaline magma either by prolonged differentiation or lowest degree of partial melting of an enriched/fertile mantle source.

Soil contamination due to heavy metals from tannery industries: A case study of Jajmau (Kanpur) and Unnao industrial areas, Uttar Pradesh, India

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Environmental geochemical studies were carried out in and around Jajmau (Kanpur) and Unnao industrial areas, to find out the extent of chemical pollution in soil due to waste disposal from tannery industries. There are more than 2500 tanneries in the country and nearly 80% of them are engaged in the chrome tanning process. In Uttar Pradesh, Jajmau (Kanpur) and Unnao (80°18' – 80°30' E longitude and 26°25' – 26°34' N latitude) are prominent centers for leather processing and there are two clusters of tannery industries (about 450) along the banks of river Ganga. Geologically the study area is covered by alluvium of Quaternary age consisting of older alluvium of middle to upper Pleistocene and newer alluvium of Holocene and the climate of the study area is semi-arid type.

Fifty-three soil samples were collected from Jajmau (Kanpur) and Unnao industrial areas from top 10 cm layer of the soil and were analyzed for heavy metals by using Philips PW 2440 X-ray fluorescence spectrometer. The data reveals that the soil in this area is significantly contaminated, and shows very high concentrations of chromium ranging from 162 to 60819 mg/kg (14535 mg/kg average). Other heavy metals such as Ba ranges 44-781 mg/kg (295.7 mg/kg average), Cu 1.7-126 mg/kg (42.9 mg/kg), Pb 22-68 mg/kg (40.4 mg/kg average), Sr 47-151 mg/kg (105.3 mg/kg average), V 1.3-209 mg/kg (54.4 mg/kg average) and Zn 44-688 mg/kg (159.9 mg/kg average). High concentrations of these toxic/heavy metals are contributors for the degradation of human health in the study area and people suffer from occupational diseases such as asthma, chromium ulcers and skin diseases. Distribution and correlation of heavy metals in soil along with possible remedial measures are discussed.

New constraints on the origin of short-lived radioactive nuclides in the early solar system

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The presence of several short-lived radioactive nuclides (⁷Be, ¹⁰Be, ²⁶Al, ³⁶Cl, ⁴¹Ca, ⁵³Mn, ⁶⁰Fe) in the early solar system is established from the presence of their decay products in constituents of primitive meteorites such as Ca-, Al-rich inclusions (CAIs). These nuclides are either (i) the products of stellar nucleosynthesis (as demonstrated by the presence of ⁶⁰Fe) and were injected in the protosolar cloud before or during its collapse or (ii) the result of interactions of energetic particles (as demonstrated by the presence of ¹⁰Be) with gas and dust either in the protosolar nebula or in the presolar cloud. As shown by X-ray observations of young stellar objects, one obvious source of an intense flux of accelerated particles in the protosolar nebula is the young active Sun. CAIs being the oldest solids formed in the solar system, they may have formed close to the young Sun and may contain a record of these irradiation processes. Understanding the origin of short-lived radioactive nuclides is thus fundamental not only for early solar system chronology but also for deciphering the astrophysical context of the formation of the first solids in the early solar system.

We report Li, B and Mg isotopic analyses by ion microprobe (Cameca ims 1270) of a set of various CAIs from the CH chondrite Acfer 182 and CV3 chondrite Efremovka, including some hibonite-rich CAIs which because of their refractory composition are considered to be among the earliest CAIs. The hibonite-rich CAIs have lower ²⁶Al/²⁷Al ratios (<1.1±0.5×10⁻⁵) than the classical type B CAIs from Efremovka (e.g. CAI E66 which has a ²⁶Al/²⁷Al ratio of 5.49±0.15×10⁻⁵). The ¹⁰Be/⁹Be ratios are lower by a factor of two in hibonite-rich CAIs compared to Efremovka type B CAIs (e.g. ¹⁰Be/⁹Be=1.2±0.3×10⁻³ in E65). These data show that ²⁶Al and ¹⁰Be are likely decoupled in the early solar system. The low ²⁶Al/²⁷Al ratios in hibonite-rich CAIs may reflect the steady state abundance of ²⁶Al in the local interstellar medium. The hibonite-rich CAIs show a systematic slight but significant ⁶Li enrichment indicative of the presence of a component produced by spallation. This can be used to put a higher limit on the amount of ¹⁰Be which could have been produced in the presolar molecular cloud by trapping of galactic cosmic rays.

Water structure and dynamics on aqueous barium ion and the {001} barite surface

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Water structure and exchange kinetics are important to a number of fundamental geochemical processes. For example, the rate of dissolution of isostructural materials often correlates with the rate of water exchange on the aqueous cation. However, thus far most computational studies have focused on structure of the mineral surface. Water structure and kinetics are less often studied, yet are necessary to understand such basic properties of the interface such as adsorption energy. In this work, we use an existing molecular dynamics potential model [1] to estimate the water structure and exchange kinetics of aqueous barium ion the barite {001} surface.

Water exchange kinetics were using a correlation function as well as the potential of mean force and a reactive flux. The latter methods involve calculating a transition state theory rate constant through integrating a free energy of activation estimated from a radial distribution function and a transmission coefficient estimated via a reactive flux. It was found that using only the barium-oxygen distance to constrain the reaction coordinate resulted in unphysical results and a solvent organization parameter is necessary. Using these methods, water structure and exchange kinetics surrounding aqueous barium ion fall within the range of experimental estimates.[2] Water-barium distances for the surface ions on the {001} barite surface are very close to those of the aqueous ion, yet the rate constant is significantly faster. This increase in exchange rate is attributed to a relatively hydrophobic, high energy interface.

The calculated water structure of the overall interface is relatively complicated, with up to five distinguishable oxygen positions interacting with both surface sulfates and bariums. This complex structure contrasts to the fit of experimental X-ray reflectivity data, which can only justifiably include a single ordered layer of water that matches unsaturated barium-oxygen bonds.[3] It is unclear at this point how to reconcile of this discrepancy, but there are substantial uncertainties in both the experimental and computational water structures.

This study is the first time the kinetics of water exchange on aqueous barium ion and barite surfaces have been examined using a reactive flux method and as such, represent a significant expansion of this new and hitherto relatively unexplored method to systems of geochemical interest.

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Continental erosion averaged over space and time

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Matching rates of denudation at all temporal scales have been used to infer erosional steady state in various mountain belts. What variation in erosion rates is significant or expected from one temporal and spatial scale to another and over a range of tectonic regimes?

Under ideal conditions, the cosmogenic nuclide flux out of a basin can be used to measure the denudation rates that average over millennia for the entire drainage area. Erosion rates measured over shorter timescales (e.g. sediment yield, reservoir infill) show greater variance due to the stochastic nature of erosion and surface process interactions. Short-term measurements miss rare events in a predictable way and because of this property, rates of surficial processes measured over increasingly longer time intervals can incorporate longer intervals of process inactivity, thus producing a different apparent rate of deposition and erosion (Sadler, 1981; Gardner *et al.*, 1987).

We use a new (available from the author) compilation of all previously published and new cosmogenic nuclide-derived denudation rates and sediment-flux measurements for the same basins to evaluate this variability. Despite anthropogenic effects, the majority of sediment fluxes are less than long-term rates of erosion, contrary to that predicted by Gardner *et al.* (1987).

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What controls Sulfur isotope fractionation in modern estuarine sediments?

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Sulfur isotopes are a promising tool for tracing sulfate reduction in sedimentary rocks, and for providing constraints on one of the oldest metabolic processes on Earth. However, the relationship between isotopic fractionation and parameters such as sulfate reduction rate, temperature and availability of organic matter remains unclear, with conflicting results from pure culture and natural population studies [1,2,3]. Here, we use flow through reactors that contain undisturbed slices of sediment to measure sulfate reduction rate under quasi-steady state conditions. Flow through experiments were run to investigate the control of temperature, sediment depth, organic matter content, sulfate concentration and the effects of inhibitors on sulfate reduction rate and sulfur isotope fractionation. Samples were collected at a brackish location of a temperate estuarine sediment (Western Schelde, The Netherlands).

Our results indicate an inverse relation between sulfate reduction rate (SRR) and sulphur isotope enrichment factor under optimum temperatures (20 and 30°C). This trend disappears at low rates (<10 nmol cm⁻³h⁻¹) and for non-optimum temperatures (10 and 50°C). Large fractionations (>20‰) were observed only at low SRR (<10 nmol cm⁻³ h⁻¹). Sediment depth as well as organic matter content did not significantly affect isotope fractionation.

This study demonstrates that the degree of isotope fractionation can be used to infer SRR in natural populations as well as in pure cultures providing that the bacterial population is thriving under optimal conditions.

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History of seafloor hydrothermal activity in the SW Pacific Bare Zone using fish teeth strontium isotope dating of metalliferous sediments

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A 2 million km² region virtually devoid of sediment has been identified in the remote SW Pacific Basin (February/March 2005 drill site survey cruise - Rea *et al.*, 2006). This region, informally termed the "South Pacific Bare Zone" comprises ocean floor dating back to the Late Cretaceous. Seismic profiling, piston cores and gravity cores reveal the full extent of barren crust – an area nearly the size of the Mediterranean Sea. Within the Bare Zone, a small (1km²) abyssal valley with 24 m of sediment was identified and sampled with a large diameter piston core, leading to recovery of 8.35 meters of metalliferous sediment at 5082 m water depth. Fish-teeth Sr-isotope stratigraphy reveals a continuous record of sedimentation 31Ma to present, with an average linear sedimentation rate at this site of 0.27 mm/kyr. However, the fish teeth age-depth profile and INAA geochemistry show an exponentially decreasing hydrothermal flux, with sedimentation rates approaching <0.05 mm/kyr between 17 Ma and the present. The origin of the main pulse of hydrothermal activity is uncertain, but may be related to a series of late Eocene/early Oligocene ridge jumps and propagating rifts that accompanied large-scale plate tectonic reorganization of South Pacific seafloor. The fish teeth Sr isotope age-depth profile and pelagic clay geochemistry also reveals that the terrigenous component at this site registers a very low eolian flux, increasing in proportion to the hydrothermal component upcore. Primary dust sources were likely Australia and New Zealand, consistent with Nd-Sr-Pb isotopes of detrital extracts. The unusual conditions of Cenozoic non-deposition that characterize this area of the South Pacific make this the first record of its kind, providing unique insight into hydrothermal activity and eolian sedimentation since the early Oligocene. The utility of the fish teeth Sr isotope method for dating marine hydrothermal cores should be explored further.

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No role for discrete, depleted high $^3\text{He}/^4\text{He}$ mantle

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Recently, several studies have shown an apparent link between high $^3\text{He}/^4\text{He}$ and depleted mantle (Stuart *et al.*, 2003; Class and Goldstein 2005) which is inconsistent with prevailing orthodoxy where high $^3\text{He}/^4\text{He}$ reflects a lack of mantle degassing and depletion. Here we present 28 new $^3\text{He}/^4\text{He}$ analyses from Tertiary picrites of Baffin Island and West Greenland and have identified 21 samples with $^3\text{He}/^4\text{He} > 35R_a$ (the highest value observed in recently erupted basalt). Whole rock $^{143}\text{Nd}/^{144}\text{Nd}$ for these samples show a significant peak at depleted values (mean of 0.513024), as observed in an earlier study (Stuart *et al.*, 2003), but an interesting feature of the new data is the scatter in $^{143}\text{Nd}/^{144}\text{Nd}$ down to 0.512876, a value which although not chondritic is certainly less depleted than that observed by Stuart *et al.*, (2003). It is important to establish the effects of crustal contamination that would act to lower both $^3\text{He}/^4\text{He}$ and $^{143}\text{Nd}/^{144}\text{Nd}$. Whole rock Pb isotope data show significant variations which are consistent with incorporation of unradiogenic Pb of crustal origin but critically there is no relationship between Pb and Nd isotopes. Thus, if crustal contamination is the cause of Pb isotope variation, it was not responsible for the range in $^{143}\text{Nd}/^{144}\text{Nd}$. In addition, major and trace element compositions of olivine hosted melt inclusions allow us to compare melt inclusion compositions from olivines of various sizes, that record different stages of magma evolution, to provide better resolution on the effects, if any, and timing of potential crustal contamination. We conclude that variations in $^{143}\text{Nd}/^{144}\text{Nd}$ are likely to derive from heterogeneity in the mantle sources tapped by the Baffin Island and West Greenland picrites and that these new data do not support the concept of a discrete depleted-high $^3\text{He}/^4\text{He}$ end-member in the mantle.

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What controls iron isotope fractionation in an acid mining pile?

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This study explores the potential use of Fe isotope analysis in long-term risk assessment of acid mine drainage generating mining piles. Balci *et al.* (2006) have demonstrated the enrichment of heavy Fe isotopes in Fe oxidation products with respect to $\text{Fe(II)}_{\text{aq}}$ during growth of *Acidithiobacillus ferrooxidans* in batch culture-experiments. They argued that inorganic equilibrium fractionation between $\text{Fe(III)}_{\text{aq}}$ and $\text{Fe(II)}_{\text{aq}}$ is the controlling reaction as described earlier by Welch *et al.* (2003). These authors have shown that in equilibrium the isotopic difference is $\Delta^{56}\text{Fe}_{\text{Fe(III)-Fe(II)}} \sim 2.9 \text{ ‰}$. Here, we present Fe isotope ratios measured on sequentially leached tailings material sampled from a 25 m drill core into an active pile at Selebi-Phikwe, Botswana, and of an additional analog column bio-leaching experiment in the laboratory. Throughout the drill core, reactive solid Fe(III) is enriched in the heavy isotopes (average $\delta^{56}\text{Fe} = -0.15 \text{ ‰}$) with respect to pyrrhotite (average $\delta^{56}\text{Fe} = -0.40 \text{ ‰}$). This is in general agreement with the batch experiments of Balci *et al.* (2006). The fraction of exchangeable and soluble Fe shows very low $\delta^{56}\text{Fe}$ values down to -2.4 ‰ . Such extreme values can only occur in a small residual pool after the majority of dissolved Fe has been removed by precipitation. Our results can best be explained if the total reaction is broken down as follows. Fe dissolved from pyrrhotite is partitioned by microbial Fe(II) -oxidation into a mixed $\text{Fe(III)}_{\text{aq}}$ and $\text{Fe(II)}_{\text{aq}}$ pool which quickly equilibrates isotopically. Precipitation of solid Fe(III) occurs with perhaps additional fractionation from the $\text{Fe(III)}_{\text{aq}}$ in the mix. Our data suggest that the mixed reservoir initially consisted mostly of $\text{Fe(III)}_{\text{aq}}$ whose $\delta^{56}\text{Fe}$ would be close to the initial pyrrhotite. The strongly fractionated residual derives from the remaining small pool of $\text{Fe(II)}_{\text{aq}}$. However, low $\delta^{56}\text{Fe}$ values cannot be sustained unless resupply of unfractionated, freshly dissolved Fe from pyrrhotite is sluggish. Although showing complex results, the bio-leaching experiments appear to confirm that the ratio of $\text{Fe(II)}_{\text{aq}}$ to $\text{Fe(III)}_{\text{aq}}$ in the fluid, and thus the overall metal sulfide oxidation activity in the pile, is the main factor that controls the isotopic composition of soluble Fe.

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The hydrothermal Wenzel deposit, South Germany: Implications for the formation of Kongsberg-type silver deposits

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The post-Variscan Kongsberg-type Wenzel deposit near Wolfach, Schwarzwald, Germany, the type locality of the Ag-Sb alloy dyscrasite, was investigated by ore microscopy, electron microprobe analysis, stable isotope and fluid inclusion analysis. Three mineralization stages could be distinguished in the vein. Whereas the first stage is a typical sulfide mineralization including galena and tetrahedrite, the second and third stage show a sulfide-poor association of Ag-Sb alloys with Fe-, Co- and Ni-arsenides and -sulfarsenides in a calcite matrix. The main ore minerals of this stage are allargentum and dyscrasite.

Seven distinct generations of calcite were distinguished. The $\delta^{13}\text{C}$ (V-PDB) and $\delta^{18}\text{O}$ (V-SMOW) values of these generations show a positively correlated trend that evolves from -13.0 to -4.0 ‰ and from 12.3 to 23.6 ‰, respectively.

Fluid inclusion data of stage I fluorite and quartz show homogenization temperatures of 100-180 °C at salinities of 17-26 wt.% NaCl eqv. Fluid inclusions in stage II calcite display similar, but more restricted values of 110-150 °C and 25-28 wt.% NaCl eqv., respectively. The stage III fluid inclusions of calcite show similar homogenization temperatures, but different salinities. Earlier Ag-Sb-alloy bearing calcite of this stage contains inclusions with salinities of 27-30 wt.% NaCl eqv., whereas later ore-free calcite crystals show lower salinities of 3-10 wt.% NaCl eqv. The initial ice melting temperatures of most fluid inclusions range between -45 and -60 °C and are typical of an H_2O -NaCl- CaCl_2 fluid.

Based on all available geochemical data and phase equilibrium constraints in the system Ag-Ca-Na-C-Si-Cl-O-H, we favor a model in which basement-derived near-neutral-pH hydrothermal fluids remobilized older Ag-Sb-bearing mineralizations. Mixing of these fluids with more alkaline formation waters from the Mesozoic cover rocks resulted in the precipitation of the silver alloys in an enrichment zone at P-T conditions of 120-150 °C and approximately 200 bars. A significant pH shift from near-neutral to alkaline is able to explain the abundant association of silver alloys with calcite gangue and the general absence of quartz in the enriched ore zone. This conceptual model can be applied to similar ore deposits world-wide, where rich ores of native silver and silver alloys are hosted by calcite-rich and quartz-poor gangue mineral assemblages.

Interpreting reaction rates at the field scale

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Interpreting reaction rates and associated rate formulations (rate constants, catalytic and inhibitory effects, reaction affinity) at the field typically requires explicit consideration of transport. This is because overall rates may be either locally transport-controlled in the case of heterogeneous systems, or even globally transport-controlled if sufficiently large length scales for reaction are considered. The potential role of physical and chemical heterogeneity has been discussed, but is still not routinely evaluated at the field scale. Heterogeneity may introduce a scale dependence to field-scale rates even in the case where the pore fluids remain far from equilibrium due to either transverse concentration (and therefore rate) gradients, or as a result of longitudinal gradients that develop where the extent of reaction is large. These two effects can be quantified in models of the field-scale system respectively by 1) comparing results from 2D or 3D representations with those from 1D continuum models, and 2) by comparing results from 1D models with those from well-mixed flowthrough reactor models. The analysis indicates that well-mixed reactor models, implicit in the so-called "Inverse Models" to the extent that they are used to determine rate constants, should be used with considerable caution at the field scale.

Another effect associated with the presence of heterogeneities that complicates the interpretation of field-scale rates has to do with the determination of hydrologically accessible reactive surface area. Some regions within the reactive domain may be largely inaccessible because of their low permeability, or mass transfer from the low to high permeability regions (where the bulk of the flow occurs) may be rate-limited. An approach that uses the retardation of a reactive tracer to quantify the hydrologically accessible reactive surface area is presented and is combined with an example involving the weathering of smectite to kaolinite at the Shale Hills site in Pennsylvania, USA.

The complexity of many multicomponent reaction networks presents another significant obstacle to the interpretation of rates at the field scale. Problems are usually manifested when an incomplete data set has been collected at the field scale, in which case potentially important pathways may be neglected altogether. In this regard, combining major and minor element aqueous and solid phase chemical analyses with isotopic analyses offers a powerful approach for delineating all of the important pathways within a field-scale reaction network. Successful examples of such an approach will be provided.

Magma sources in the Icelandic Western Rift Zone (WRZ): Crustal and mantle input

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Low $\delta^{18}\text{O}$ Icelandic rift basalts have been interpreted as a result of contamination by low $\delta^{18}\text{O}$ crust, or as derived from an unusual, low $\delta^{18}\text{O}$ mantle source. In the Reykjanes Peninsula (RP) $\delta^{18}\text{O}_{\text{OL}}$ values $\geq +4.2$ ‰ have been interpreted as mantle derived, while lower values were thought to reflect contamination [1]. ($^{230}\text{Th}/^{238}\text{U}$) disequilibrium has also been used as an indicator of crustal contamination in both rift, and off-rift zones in Iceland [2]. Since the magnitude of ($^{230}\text{Th}/^{238}\text{U}$) disequilibrium varies radially with proximity to the proposed centre of the Iceland plume [3], variations in ($^{230}\text{Th}/^{238}\text{U}$) may however, reflect melting parameters rather than crustal contamination.

The WRZ is an ideal area to study the extent to which low $\delta^{18}\text{O}$ and ($^{230}\text{Th}/^{238}\text{U}$) disequilibrium indicate crustal contamination, due to their eruption during post/last-glacial time minimizing the need for an age correction. Further, the rift zone is orientated tangentially to the assumed location of the centre of the plume, and thus variations in extent of disequilibrium cannot be strongly controlled by distance to the plume.

A study of new O-Sr-Nd-Pb data from the WRZ demonstrates $\delta^{18}\text{O}$ as low as $+3.79$ ‰ in primitive lavas (9.5 % MgO, $^{143}\text{Nd}/^{144}\text{Nd}$ 0.513046). The WRZ data appear compatible with varying degrees of crustal contamination in terms of $\delta^{18}\text{O}$ and $^{143}\text{Nd}/^{144}\text{Nd}$. However, assuming the WRZ assimilant has a $\delta^{18}\text{O}_{\text{OL}}$ of $+1.2$ ‰ [1] then 35 % bulk assimilation is required to produce the lowest $\delta^{18}\text{O}_{\text{OL}}$ sample of 3.79 ‰ from the mantle mean of 5.2 ‰ $\delta^{18}\text{O}_{\text{OL}}$. This is difficult to reconcile with the relatively low degrees of fractional crystallization, shown by the 9.52 % MgO found in this sample.

Isotopic data from Hengill central volcano, located at the triple junction between the WRZ, RP and the south Iceland seismic zone (SISZ), plot at the enriched end of WRZ Nd-Sr-Pb trends, showing the sources are isotopically linked. $\delta^{18}\text{O}_{\text{OL}}$ from Hengill is $3.83 - 4.5$ ‰, with $5.91 - 8.73$ % MgO. This range is present in rocks with homogenous Nd-Sr isotope ratios, showing that Hengill is much more consistent with assimilation producing the low $\delta^{18}\text{O}$ signature.

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The hydrolysis and chloro complexation of iron(III) in hydrothermal solutions

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A knowledge of the stability of iron(III) hydroxide and chloride complexes in hydrothermal solutions is important for quantitative interpretation of the transport and precipitation of iron by crustal fluids. It is generally accepted that iron is predominantly transported as iron(II) species in reduced hydrothermal fluids in the Earth's crust. However, boiling (phase separation) occurs ubiquitously in hydrothermal systems with the partitioning of hydrogen into the volatile (less dense) phase. The redox state of the residual liquid (or denser phase) and pH changes, such that iron(III) may become the predominant oxidation state of iron. A knowledge of the complex equilibria involving Fe^{3+} is therefore important in understanding the transport and precipitation chemistry of iron by fluids in the crust at high temperatures and pressure.

The complexation of iron(III) with hydroxo and chloro ligands has been studied as a function of solution composition (salinity and pH) in hydrothermal solutions to 300°C at saturated water vapour pressure. Two experimental methods have been applied, uv-vis spectrophotometry using a high-temperature, flow-through gold-lined optical cell and hematite solubility using flow-through and static autoclave systems. The strong ligand-to-metal charge transitions of the uv-vis spectra of iron(III) hydroxo and chloro complexes at wavelengths below 400 nm were used to obtain molar absorptivities, ϵ , and equilibrium formation constants using principle component analysis and non-linear least squares treatment of the hematite solubility measurements were used to obtain solubility constants. Based on the experimental result iron(III) was found to hydrolyse to form FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3(\text{aq})$ and $\text{Fe}(\text{OH})_4^-$ with increasing pH and FeCl^{2+} , FeCl_2^+ , $\text{FeCl}_3(\text{aq})$ with increasing chloride concentration in acid solutions. Iron(III) hydroxide complexes were found to predominate in dilute and alkaline hydrothermal solutions whereas with increasing chloride concentration and temperature iron(III) chloride complexes become increasingly important species in oxidised acid solutions.

A 3.3 Ga Mo-Cu porphyry-style deposit at Spinifex Ridge, East Pilbara, Western Australia: Re-Os dating of Paleoproterozoic molybdenite

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Here we show that the Re-Os chronometer is robust for Paleoproterozoic molybdenites. Prior to this study, AIRIE's oldest dated molybdenite was from the 3128 ± 13 Ma Sergeevskoe porphyry Au-Cu-Mo deposit, Ukraine. The youngest is from the 2.120 ± 0.007 Ma Boyongan porphyry Cu-Au deposit, Philippines. Thus, molybdenite chronology can be readily used across the full span of geologic time [1].

The Spinifex Ridge (Coppins Gap) Mo-Cu deposit is located immediately north of the variably deformed Mount Edgar batholith in the 3.52-2.85 Ga East Pilbara granite-greenstone terrane. Mo-Cu mineralization, estimated at 481 million tons carrying 0.06% Mo and 0.08% Cu, is associated with high-level quartz-plagioclase porphyry intruded into Warrawoona Group basalts and rhyolites, and porphyritic granodiorite bodies [2]. Quartz veins with molybdenite and chalcopyrite are most abundant where both granodiorite and quartz-plagioclase porphyry are present.

Two molybdenite samples ascertain the timing of porphyry-style Mo-Cu mineralization at Spinifex Ridge. The drill core samples (SRD053, 227.2 and 227.6 m) represent main-stage stockwork ore hosted in potassically altered porphyry. Molybdenite was analyzed by NTIMS using a Carius tube digestion and double Os spike. Re-Os ages are 3298 ± 11 Ma for a 1.5 cm quartz vein with irregular molybdenite selvages and 3284 ± 11 Ma for a 0.2 cm molybdenite clot adjacent to a similar vein. Ages are indistinguishable within their 2-sigma uncertainties, and agree with SHRIMP U-Pb zircon ages [3] for the Mount Edgar batholith (3314 ± 13 Ma, Coppin Gap suite; 3304 ± 10 Ma, Boodallana suite).

Ore zone geometry inclusive of silicified, brecciated borders to the quartz-plagioclase porphyry suggest that the entire intrusive-mineralization system was strongly tilted by regional listric faulting that accompanied uplift of the batholith. The Re-Os dates present a maximum age for that faulting and a minimum age for the hosting quartz-plagioclase porphyry. The geology supports formation of the Spinifex Ridge Mo-Cu deposit in a weakly extending brittle regime at ~ 3.3 Ga, similar to magmatic-tectonic conditions that produce Mo-Cu porphyry-style deposits today.

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Atlantic cold-water spells into the Mediterranean caused the abrupt changes in the Levant's post-Glacial hydrology and human-culture development

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Intrusion of cold Atlantic-water to the east Mediterranean at the 14th millennium BP (e.g. "melt water pulse MWP1-A") caused the abrupt drop of Lake Lisan (the last glacial precursor of the Dead Sea) from its maximum MIS2 stand of ~ 160 m (below mean sea level) to its lowest level (< 500 m bmsl), marking the severest catastrophic aridity that prevailed in the late Quaternary Levant. Regional rains resumed and lake level rose during the Younger Dryas (13 millennium BP) but dropped sharply again during the 11th millennium BP (reflecting "melt water pulse MWP1-B").

While the "melt-water pulses" amplified the post-glacial warming trend in the Levant, causing extreme aridities, the NA-cooling of the YD imposed a strong deviation from this trend. It seems that the YD cooling lags after the melt water pulses by causing shifts in the Polar fronts and Westerlies that brought more rain to the Levant.

The abrupt changes in the Levant climate led the major developments in the regional cultural evolution - the collapse of the Natufian culture and the rise of the Pre-Pottery Neolithic (PPN) culture and agriculture society upon the transition to the milder Holocene.

The rapidity of the response of the regional hydrological systems to the global climate changes and the sensitivity of past human cultures to these changes are certainly important lessons and alarming signals for our human society.

UV femtosecond laser ablation applied to stable Fe isotopes in BIFs

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Here we present *in situ* stable Fe isotope measurements in Precambrian banded iron formations (BIFs) using our in-house built laser ablation system which consists of a frequency-quadrupled fs laser operating at a wavelength of 196 nm and a multicollector-ICP-MS. The short pulse length turns the ablation process away from thermal pathways preventing artificial fractionation and minimizing matrix dependency (Horn and von Blanckenburg, 2007). The accuracy of this method has been verified for different types of matrices giving a reproducibility of 0.1‰ (2SD) for the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio (Horn *et al.*, 2006). BIFs are fine-grained chemical sediments which are the product of initial precipitation from seawater and subsequent diagenetic and metamorphic processes. All of these processes involve redox reactions, dissolution and precipitation of Fe resulting in fractionation of Fe isotopes. In order to investigate these processes, we have determined the Fe isotope composition of single Fe-oxide and Fe-carbonate crystals by spot analyses at 30 microns resolution in different thin sections of low-grade metamorphosed BIFs. Small-scale isotopic variations of up to 0.9‰ in $\delta^{56}\text{Fe}$ within single layers exist for hematite as well as for magnetite. Furthermore we detect isotopic zonation in magnetite crystals as small as 30 microns which becomes heavier in their Fe isotope composition towards the rim. These heterogeneities suggest variable relocation of Fe on a sub-millimeter scale during diagenesis and metamorphism. Fe-carbonates have also been investigated. Although crystal sizes are often less than 25 microns and Fe contents are low giving only low Fe signal intensities, we have found that variations in chemical composition have little influence on the Fe isotopic composition. Both, Fe-oxides and Fe-carbonates show constant average Fe compositions over all layers within a thin section. Since also magnetite and Fe-carbonate exhibit a constant relative difference of ca. 0.9‰, either a diagenetic process with the same precursor material must have established these isotope equilibrium fractionations or, alternatively, fluid sources were distinct but pathways to the Fe-carbonate and Fe-oxide were steady with time. These results illustrate that the study of stable Fe isotopes at high spatial-resolution have the potential to gain a better understanding on the mechanism of BIF formation and the Precambrian Fe cycle.

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Potassium partitioning in the lowermost mantle from ab-initio computations

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Partitioning of radioactive isotopes in the Earth's interior is of great importance to the thermal and dynamic state and evolution of the Earth as radioactive decay provides an important source of energy for mantle dynamics. As a consequence, enriched (or depleted) reservoirs in the mantle can influence the energy balance in geodynamics. The recently discovered phase transition in MgSiO_3 from perovskite (pv) to post-perovskite (ppv) in the lowermost mantle provides the possibility for an enriched or depleted zone at the base of the mantle. Therefore, the partitioning of radiogenic isotopes among the phases of the lower mantle is of central importance in geochemistry and geodynamics of the deep Earth. Here we take a first step in addressing this issue by considering the partitioning of potassium between pv and ppv by performing *ab-initio* computations.

We have set up computations for a coupled substitutions of K and Al or Fe^{3+} (**M** ion) for 2 Mg on the A site, and evaluate the energetics of a $(\text{Mg}_{30},\text{K},\text{M})\text{Si}_{32}\text{O}_{96}$ composition in the pv and ppv structure. We compare the energetics of the following reactions for both pv and ppv to compute the enthalpy of formation:



The computations are performed with the VASP package using the projector augmented wave method for the static lattices of the high pressure phases in the reaction above. We use the generalized gradient approximation to the exchange and correlation potential. Structures are optimized for internal and external degrees of freedom at constant volume, and we assume that the **M** and K ions are at A positions directly adjacent to one another. Computations are performed for a wide compression range, reaching pressures of the CMB.

Slightly above 100 GPa we predict that $D_K < 1$, implying that K partitions preferably into the ppv phase. Increased temperatures would decrease the magnitude of preferred differentiation. This makes a K enriched layer at the base of the mantle a possibility. It is clear, however, that the effect of other phases stable in the lower mantle (Ca-pv and mw) must be considered in a full assessment of K distribution in the lower mantle.

Biogeochemical cycling of rare earth elements in surface soils

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Stille *et al.* (2006) have suggested in a study on the Strengbach catchment in the Vosges mountains (eastern France, <http://ohge.u-strasbg.fr>) that preferential absorption of light REE (LREE) by vegetation may contribute to LREE depletion of stream water. New REE data on soil solutions recovered on the same site from 10 to 70 cm depth show similar to vegetation an enrichment of the LREE. Strontium and neodymium isotope data from these solutions indicate that up to 90 % of Sr and Nd are derived from vegetation litter. This origin of the REE in the surface soil is in strong contrast to the underlying regolith, where the mobile REE essentially originate from the dissolution of apatite derived from the granitic bedrock (Aubert *et al.*, 2001). The Sr isotope record from tree rings of 3 spruce specimens planted 90-100 years ago on the study site yields valuable information on the formation of these different REE pools. The data demonstrate that the spruce mainly absorbed Sr from granite-derived minerals during the first years after plantation. But rapidly the isotopic compositions of the tree rings are shifted to values typical for atmospheric deposits. We interpret this evolution by transformation of the initial mineral soil into a surface soil rich in organics issued from the decomposition of vegetation litter. This new surface soil contained in the beginning mainly regolith-derived Sr inherited from vegetation. This initial Sr was then continuously removed by soil water runoff and replaced by atmospheric Sr. We are actually analyzing Nd isotopic compositions on the same spruce samples in order to confirm this hypothesis for the REE. This scenario thus suggests that vegetation and surface soil form an almost closed biogeochemical cycle for the REE, accumulating preferentially LREE issued from vegetation litter. This cycle is modified by inputs from atmospheric sources and leaching of remaining soil minerals, and outputs by surface and soil water runoff. Local stream water is in contrast to surface soil and vegetation depleted in LREE indicating that surface soil water is not the dominant source for stream water. This is in agreement with Nd-Sr isotope data from Stille *et al.* (2006) showing that stream water REE are mainly derived from alteration of apatite within the mineral soil. We suggest that the formation of a LREE enriched reservoir in the surface soil has together with preferential scavenging of the LREE by adsorption and precipitation during groundwater flow contributed to the formation of a LREE depleted groundwater pool within the underlying regolith. This groundwater is the main source for stream water at low stream flow.

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The mobility of actinides and ⁹⁰Sr from bomb test fallout in a karstic area, Jura Mountains (Switzerland)

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The presence of artificial radioisotopes of plutonium, americium and strontium is mainly due to the atmospheric tests of nuclear bombs before 1964. Present day inventories of these radionuclides in soils of the Jura Mountains (Switzerland) often are less than expected. Apparently, there has been leakage from the soils (especially the thin soils) into the karst of this region of carbonate rocks.

With the goal to assess this possible long-range migration in a natural setting we analyzed the radioisotopes

- in upland soils (soil profiles and soil solution profiles near Col de Mollendruz, Switzerland, 1200 a.s.l.),
- in a karstic source at a distance of ca. 5 km (water and aquatic mosses, 660 m a.s.l.), and
- in cave deposits from the same area.

The mean soil inventories (0-25 cm) for thick soils are 1.3 kBq/m² and 0.12 kBq/m² for ⁹⁰Sr and Pu, respectively. The radioisotopes have significantly diffused towards deeper soil layers (40 cm depth or more) and they are also present in measurable amounts in the soil solution (< 0.22 µm, i.e. dissolved and colloidal). These findings highlight the potential of long-range transport in colloidal form. The calculated distribution coefficients K_d are on the order of 10'000; 3'000; and 1'500 for Pu, Am, and Sr, respectively.

The radioisotopes appear in the waters of the karstic source and in aquatic mosses collected close to the source. The plutonium activity found in the filtered (<0.45 µm) source water is 4 and 22 µBq l⁻¹ (U₉₅ = ±25 %) at high-stand and low-stand, respectively. The Sr-90 activity of these waters is approximately 1000 times higher. In the mosses we find up to 20 mBq/g or more of Sr-90. However, most of this activity is associated with carbonates, which have precipitated on the mosses after degassing of CO₂ from the source waters. The Pu activities of the moss samples vary between 0.1-0.2 mBq/g.

Taken together our results demonstrate the long-range transport (km-scale) of Pu, Am, and ⁹⁰Sr in a natural karstic environment with no radioisotope contamination other than "global fallout".

Solute exchange across the sediment water interface in an acidic pit lake

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Solute exchange across the sediment-water interface affects the water quality in mining pit lakes. Fluxes are supposed to be affected by advective groundwater flow. However, benthic solute fluxes in such lakes have mostly been determined by sediment core incubations in the laboratory or by calculation from pore water profiles.

In the present study direct solute flux measurements were carried out *in situ* in acidic Mining Lake 111 in the Lausitz lignite mining area, Germany. Three sites were chosen to represent A) groundwater inflow conditions B) the lake profundal and C) a reference littoral site. A volume of lake water and the sediment below were enclosed using an opaque benthic flux chamber. Oxygen decrease in the chamber was directly measured using an optode, whereas parameters such as total inorganic carbon (TIC) and dissolved Fe²⁺ were analyzed in a series of water samples withdrawn from the chamber.

Sites B and C showed oxygen consumption rates between 5 and 15 mmol m⁻² d⁻¹ while oxygen loss from the chamber at site A equaled rates between 19 and 35 mmol m⁻² d⁻¹. TIC fluxes from the sediment varied closely around 5 mmol m⁻² d⁻¹ at sites B and C, but reached up to 100 mmol m⁻² d⁻¹ at site A. Further a distinct increase of ferrous iron in the chamber was detected only at site A, i.e. in the groundwater inflow area.

Our results reveal significant differences in benthic solute fluxes depending on groundwater inflow and setting in the lake. The groundwater inflow area is characterized by high oxygen consumption and high inflow of TIC and dissolved iron. To our knowledge these are the first measurements of this kind, providing valuable practical experience for the use of benthic flux chambers in pit lake research.

FTIR water observation in minerals from diamond inclusions and matrix of diamondiferous eclogite

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The series of recent observations have recovered that nominally anhydrous minerals (NAM) in the Earth's mantle may contain significant amount of water. There are some evidences that water plays an important role in diamond formation. Here we present the first data on water content in clinopyroxenes (Cpx) in the matrix and diamond inclusions (DI) from diamondiferous eclogite xenolith from Udachnaya kimberlite pipe (Yakutia, Russia, description in [1]). The water content has been estimated from unpolarized FTIR spectra of slices of the rock and polished plates of diamonds with DI. Spectra from individual DI have been obtained by subtraction to diamond absorption in the point near inclusions. The thickness of rock slices was measured by micrometer and thickness of inclusions was determined by up and bottom focusing under microscope with reference to refractive index.

The strong band at 3450 cm⁻¹ and two weaker bands at 3620 and 3740 cm⁻¹ are observed in FTIR spectra of Cpx from the matrix of eclogite. Most Cpx inclusions in diamonds show single absorption band at 3450 cm⁻¹ and only one inclusion has additional band with the maximum at 3600 cm⁻¹ (may be attributed to OH band in chlorite [2]). Water content in Cpx has been estimated by using calibrations from [3]. Water concentrations are 60-90 ppm in Cpx from the matrix and 80-150 ppm in Cpx from diamond inclusions. Neither Grt DI nor Grt from the matrix do not show any water absorption in their FTIR spectra.

Specific results of this study are: (i) the major phase containing water in the eclogite is Cpx; (ii) water content in the matrix and DI from eclogite is not significantly different. It may testify that water content in eclogite did not change during period between diamond formation and ascent of xenolith to the surface by kimberlite magma.

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Towards improved accuracy of SHRIMP zircon ^{207}Pb - ^{206}Pb measurements

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SHRIMP and other ion probes are routinely utilized to determine $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of zircons, but only in special cases can the accuracy of the measurements be claimed to be better than a few ‰. A great deal of attention is placed on calibrating $^{206}\text{Pb}/^{238}\text{U}$ ratios, yet for $^{207}\text{Pb}/^{206}\text{Pb}$ this is seldom the case. Any systematic bias in $^{207}\text{Pb}/^{206}\text{Pb}$ of zircon is considered insignificant relative to the low precision of the individual spot analyses, a reasonable assumption based upon the generally well-known characteristics of the large ion probe. Nevertheless, as several individual $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ measurements are typically pooled to improve overall precision to the $\pm 1\text{-}5$ ‰ level for Paleoproterozoic or older zircons, the accuracy of the composite ratio should be a concern.

There are several potential sources of bias in ion probe $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ measurements of zircon, including instrumental mass fractionation, peak shape, detector performance, isobaric interferences, common Pb correction, and the method of data processing. Although it is important to understand and potentially control these individual factors, it is critical to be able to measure the overall bias. Unfortunately, there appear to be no ion probe zircon reference materials developed expressly for $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ calibration. Our data obtained from analyzing the Proterozoic U-Pb zircon QGNG suggest that systematic errors of several ‰ may exist between sessions on the same instrument and between different instruments. However, this zircon is not a suitable Pb-isotope standard for several reasons, and the validity of the results is uncertain. We have developed an Archean (ca. 3.5 Ga) $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ zircon reference material, and TIMS data indicate homogeneity. The goal is to incorporate analyses of this material as a routine part of SHRIMP zircon sessions in order to monitor and potentially correct for any systematic error in the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ages.

Crustal anatexis in the early Archean: Geochemical and isotopic evidence from the ca. 3.66 Ga Nuvvuagittuq Tonalite Suite

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Geochemical and Nd isotope data are presented for a suite of ca. 3.66 Ga tonalites from the 3.8 Ga Nuvvuagittuq supracrustal sequence in the Inukjuak Domain in the western Minto Block, northeast Canadian Superior Province. The Nuvvuagittuq volcano-sedimentary sequence consists of mafic amphibolites with ultramafic lenses, and intermediate and felsic schists dated at ca. 3.8 Ga and interpreted to be of volcanic origin. The sedimentary rocks consist of conglomerate, banded iron formation and quartzitic iron formation. The supracrustal assemblage has a semi-oval form and the tonalite suite both mantles the exterior of the oval and forms the inner core of the assemblage. The exterior sheath of the tonalite is mylonitized and in tectonic contact with Neoproterozoic (2.7-2.8 Ga) tonalite suites of the Inukjuak Domain. The tonalite core is less mylonitized but both the marginal and core portions of the suite vary from tonalite to granodiorite and granite in composition.

A Lu-Hf isochron mineral-whole rock isochron from the tonalite core yields an age of 3645 ± 26 Ma which is the same age, within error, of the 3.66 Ga U-b zircon age from the tonalite sheath. The tonalite suite is characterized by light Rare Earth element (REE) enriched profiles and variable heavy REE depletion as well as high La/Yb (n) and moderate Sr/Y ratios at low Yb and Y concentrations. Initial Nd and Hf isotopic values are largely negative suggesting that the suite was formed by melting of an older crustal component. Comparison with the isotopic evolution of the Nuvvuagittuq supracrustal sequence suggests that the tonalites may have formed by crustal anatexis of the 3.8 Ga supracrustal sequence. The tonalite suite represents the oldest tonalite suite in the Superior Province and compares in age with anatectic melting events described in the Eoarchean gneisses of West Greenland (e.g. Amitsoq gneisses) and Labrador (e.g. Uivak Gneisses) of the North Atlantic Craton (NAC). The commonality of the ca. 3.66 Ga anatectic event may imply a widespread Early Archean migmatization event.

Fungal transformation of lignite in overburden dumps

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Acidity in overburden dumps of open cast lignite mines poses a considerable environmental threat. Despite the persistence of the dump organic material (lignified organic matter), microbial acidity attenuation processes such as iron sulphide formation by microbial sulphate reduction were observed within several dumps (Storch *et al.*; 2007). Fungi are known for their ability to liquefy lignite (Ward; 1985). Therefore, autochthonous acidotolerant fungi may provide bacterial substrates by transformation of lignite into water soluble organic matter.

Methods

Autochthonous fungal strains were isolated from dump material of the Plessa field site (Lusatia, Germany). The sediment was placed on Sabouraud glucose agar and incubated at 20°C. After formation of a thick hyphae mat identical dump material was placed on this mat. A few days later bioliquefaction of lignite particles started.

Results

The autochthonous fungus (*Mucor hiemalis*) transformed lignite particles into black and shiny droplets of very high organic carbon contents (~15 g/L). The liquid product was analysed by gel chromatography to consist of humic substances (a), building blocks (b), low molecular weight substances (c), neutral substances (d), and polysaccharides (e). The liquefied organic matter is highly polar and water soluble. HPLC analysis (Schmalz *et al.*; 2002) of the water dissolved droplets revealed the predominance of carbonylic and carboxylic functional groups. Carbonic acids are well known substrates for sulphate reducing bacteria (Widdel; 1988).

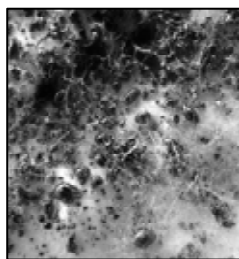


fig. 1: liquefied lignite

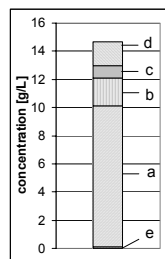


fig. 2: DOC fractions

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Isotopic fractionation of Uranium in low-temperature environments

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Uranium is the heaviest naturally occurring element and mass-dependent isotopic fractionation between ²³⁵U and ²³⁸U, which scales with $\delta M/M^2$, is not normally considered significant given the small ~1% difference in mass. It is therefore usual to assume that ²³⁸U/²³⁵U is constant in the terrestrial environment and equal everywhere to 137.88 at the present day. Importantly, isotopic fractionation of the very heavy elements has recently been investigated for mercury and thallium in the context of mass-independent nuclear field shift effects¹, which do not scale with $\delta M/M^2$, and are predicted to have permil-level effects on the heavy masses, including uranium.

We have developed experimental protocols for the precise measurement of ²³⁸U/²³⁵U and ²³⁸U/²³⁴U by multiple-collector ICPMS (MC-ICPMS) to investigate potential isotopic fractionation in uranium. Using multiple-Faraday protocols and a high-purity ²³³U-²³⁶U double spike to internally monitor instrumental mass bias effects, we are able to resolve variations in ²³⁸U/²³⁵U and ²³⁸U/²³⁴U at the 0.4 and 0.3 epsilon level (2 σ ; 1 epsilon = 1 part in 10,000), respectively. Measurements for samples formed in a range of low-temperature environments reveal sizeable, permil-level natural variability in ²³⁸U/²³⁵U². Present experiments are focussed on the isotopic fractionation of uranium during the biologically-mediated reduction of U(VI) to U(IV).

Our new observations indicate that uranium isotopic fractionation of ²³⁸U/²³⁵U may offer the potential to monitor biological pathways and redox processes occurring during mineralization, weathering, and the transition between the U(IV) and U(VI) oxidation states, offering new insight into the processes at work. Moreover, variability in ²³⁸U/²³⁵U will have a direct bearing on the U-series and U-Th-Pb chronometers, when applied to samples formed in low-temperature environments, as these chronometers currently assume an invariant ²³⁸U/²³⁵U equal to 137.88.

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Rivers of North Rhine Westphalia – Revisited

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In the early nineties of the last century rivers of North-Rhine Westphalia were examined by Veizer and members of his working group (Flintrop *et al.*, 1996). Their motivation for having a close look on these – and on other more eminent – rivers was primarily the search for the missing carbon-dioxide sink. In addition, they provided a documentation of the pollution situation. We revisited some of these rivers, looking for possible changes that occurred during the past 15 years, and visited additional rivers with the focus not on the carbon budget but more on the pollution state.

In order to isolate occurring in-river processes and to identify sources of river constituents we analysed the isotopic compositions of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water, $\delta^{13}\text{C}$ of dissolved inorganic carbon, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulphate, and $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate. Isotopic work was supplemented with measurements of common physical parameters and concentrations of major anions and cations.

The different geographic settings of the rivers are mirrored by their isotopic composition of water. Respective regional trends are affected by processes as evaporation and mixing of different water masses. Compared to previous work, salt pollution (i.e. ions commonly attributed to an anthropogenic origin) has decreased. This holds true especially for potassium and nitrate, but also for sodium and chloride. The isotopic composition of nitrate in the river Ruhr identifies organic fertilizers and sewage as the main sources, with some evidence for denitrification processes. Compared to 1991, sulphate concentration has increased in the downstream part of the Lippe. Low $\delta^{34}\text{S}$ values suggest a higher contribution from pyrite oxidation as the likely cause. This could indicate changes in mining activity and related groundwater hydrology. For dissolved inorganic carbon we found higher concentrations characterized by lower $\delta^{13}\text{C}$ -values in all rivers compared to results from the early 1990s, caused by differing meteorological situations and in-river carbon cycling.

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Cosmogenic nuclide calibration – A progress report from the CRONUS project

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One goal of the overall CRONUS project (CRONUS-Earth, CRONUS-EU and contributors from countries outside the US and EU) is to derive cosmogenic nuclide production rates from well-characterised geologic sites. We aim to generate a network of natural calibration data that span a wide range of altitudes, latitudes and exposure periods, including as many nuclides and target minerals as possible at each site. This talk will provide a status report on geological calibration of ^{10}Be , ^{26}Al , ^{36}Cl and ^3He production rates, reviewing published data and presenting initial CRONUS results from sites in North America, Scotland and Antarctica.

The geological calibration effort is closely integrated with work on altitude-latitude scaling schemes, which provide the framework for comparing production rates between different latitudes, altitudes and exposure periods. All published scaling schemes can reconcile existing ^{10}Be calibration data to within approximately 10% (1 sd). Assigning appropriate scaling errors is more complicated, however, because examination of the misfit between scaled production rate estimates and calibration data shows that there are systematic effects (biases in latitude and/or altitude) for all calibration schemes, as well as random error. The systematic component is minimal close to calibration sites, but may be large (and is unknown) at latitudes and altitudes far from calibration data. Additional calibration sites are needed to provide denser coverage, especially in latitude and exposure duration. Low latitudes are poorly represented in the data so far, and old sites are required to test the predictions of time-dependent scaling schemes which attempt to correct for paleomagnetic variations.

Age of magnetite–apatite deposits and geochemistry of host rocks, Bafq District, Central Iran

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Major hydrothermal/metasomatic Kiruna-type REE-apatite-magnetite ores (2×10^9 t) of the Bafq district in East Central Iran are hosted by Early Cambrian rhyolitic rocks and occur locally also in late spilitic basalts. This intimate association within a 150 km N–S striking structural zone, bordered by crustal faults, suggests a genetic link between magma generation and ore formation. The exact age of the mineralization, however, has not yet been determined. The tectonic setting of granitoids and rhyolites has been controversially discussed (rift setting versus magmatic arc environment) with Ramezani and Tucker (2003) favoring a collisional setting based on the chemical signature of the felsic magmatic rocks and paleogeographic reconstructions.

Our current study deals with the age of the mineralization and the geochemistry of the host rocks.

Petrographic investigations indicate that the rhyolites have been subjected to a broad-scale alkali metasomatism and an ore-related metasomatism that have modified their original composition, thus complicating the interpretation of geochemical data. Indeed, our major and trace element data do not yet permit an unambiguous interpretation of the geotectonic environment. However, we note that volcanism in the southern sector of the Bafq district is essentially bimodal with intermediate (andesitic) rocks being rarely encountered and mafic rocks being subordinate to felsic ones.

Clear apatite crystals were separated from three apatite–magnetite deposits. The nine analyzed samples yield apparent $^{206}\text{Pb}/^{238}\text{U}$ ages between about 527 and 539 Ma and thus fall entirely within the age range of the felsic magmatic rocks dated by Ramezani and Tucker (2003) [525–547 Ma]. This confirms field evidence that the ore formation was closely related to the Early Cambrian magmatic event (Daliran, 2002).

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Tracing the mineralogy of oceanic basalt sources

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Subduction of oceanic crust has introduced considerable quantities of basalt into the Earth's mantle, which, in the form of eclogite or pyroxenite, have often been proposed to constitute part of oceanic basalt sources. Isotopic evidence for mafic constituents in oceanic basalt sources remains ambiguous because their inferred isotopic composition is highly model dependent. Identification of pyroxenite derived melts on the basis of their major element composition is complicated by second order processes, i.e. fractional crystallization. Incompatible trace element compositions, however, are less affected by small extents of fractional crystallization. In addition, the higher modal abundance and different composition of garnet and clinopyroxene in pyroxenite compared to peridotite can lead to different partitioning behavior of the incompatible trace elements, which may be a useful tracer of pyroxenite versus peridotite derived melts. On the basis of recent partitioning experiments, bulk D values for pyroxenite are, on average, about a factor of 3–6 higher than for garnet peridotite. The relative compatibility of the lithophile trace elements, however, is broadly similar. The main differences are an order of magnitude higher Ba/(Th, U, Nb, La), and about a factor of 2–3 lower Nb/(Th, U, La) and Sr/(Nd, Hf, Zr, Pb) bulk D ratios in pyroxenite compared to peridotite. Owing to the extremely low bulk D values of the most incompatible elements Ba, Th, U, Nb and La, however, even large differences in their bulk D ratios result in no resolvable differences in derivative melt compositions at melt fractions $\geq 5\%$. For the more compatible elements Sr, Nd, Hf, and Zr, partition coefficient induced differences (higher Sr/(Nd, Hf, Zr) and Nd/Hf ratios) persist up to melt fractions of 20–30%. Whether differences in melt composition owing to the different partitioning behavior of garnet-peridotite and pyroxenite can be identified therefore depends largely on the style of melting and melt aggregation, i.e. how do melts form, what degree of melting is reached before separation from the solid (melt extraction) and how and to what extent do melts pool to form the aggregate melts erupted on the surface. Owing to its lower solidus temperature, pyroxenite starts melting deeper than peridotite. Key parameters for being able to resolve partitioning induced differences in melt compositions are therefore the extent of melting of pyroxenite before the onset of peridotite melting and the extent to which early pyroxenite melts can be extracted, if at all, without being significantly mixed with melts from the ambient peridotite. Regardless of the exact melt extraction scenario, the large extents of melting expected for pyroxenite ($>20\%$) suggest that any partition coefficient induced differences between peridotite and pyroxenite melts are likely to be subordinate to initial compositional differences.

Mineralogical and ore-petrographic investigation of the iron ore occurrence of Ano Valsamonero, Rethymno (Crete)

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Numerous iron ore occurrences appear within the Phyllite-Quartzite-Series (PQS) of Crete, some of which were occasionally mined. The PQS forms the lower part of the Phyllite nappe, which with Gypsum-Rauwacke-Formation, composes the Phyllite nappe of Crete that includes the metamorphic rocks between the Plattenkalk-Series underneath and the Tripolitza-Series above. The PQS contains mainly phyllites and quartzites, in addition to metaconglomerates, marbles, calcareous phyllites and metabasalts.

The examined occurrence is located about 15 km southwest from Rethymno next to Ano Valsamonero and occurs in the form of lenses within the phyllite and quartzite of the PQS. Sampling took place along a 10 m thick profile, in distances approximately 1 m in vertical arrangement. X-ray diffraction and ore microscopy were used for determination of the mineralogy and structure of the iron ore, while the chemical composition was determined by X-ray fluorescence.

The iron ore consists predominantly of hematite, goethite and quartz, and subordinately of chlorite and muscovite. Hematite occurs in the form of radial, or more rarely in punctate aggregates between the quartz grains of ferruginized quartzite, especially in those samples, which originate from the above layers of the profile. In the samples from the middle and lower parts of the profile, hematite and goethite form a ferruginized front, which replaced largest part of the groundmass of quartzite. The Fe-rich solutions penetrated quartzite and precipitated as goethite, which forms concentric textures. The goethite changes gradually by dehydroxylation into hematite. The replacement by the Fe-rich solutions takes place from hair-cracks of the existing quartz grains. The composition of the iron ore along the profile varies regarding the Fe₂O₃ and SiO₂ contents within a wide range.

According to the microscopic investigation of the ore, it is concluded that the processes, which have caused the massive replacing ferrugination of the ore occurrence of Ano Valsamonero are of epigenetic origin and can be classified to the continental ones.

Multiple sulphur isotopes reflecting compositional changes in Earth's early atmosphere

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Pyrite extracted from more than 120 samples collected from Archean and Paleoproterozoic siliciclastic sedimentary units in southern Africa, western Australia, south-central Canada as well as in southwest Greenland and ranging in age from 3.8 to 2.1 Ga display nonzero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values. Based on empirical and experimental data as well as respective modeling results, non mass-dependent sulphur isotope fractionations are considered to result from photochemical reactions of different sulphur-bearing compounds in the atmosphere under low atmospheric oxygen abundances (e.g., Farquhar *et al.*, 2000; Farquhar and Wing, 2003; Pavlov and Kasting, 2002).

The record of newly obtained non mass-dependent sulphur isotope results displays distinct temporal variations in their magnitude. High-magnitude $\Delta^{33}\text{S}$ values for the Paleoproterozoic are followed by a somewhat attenuated $\Delta^{33}\text{S}$ signal in the Mesoproterozoic, while the Neoproterozoic and early Paleoproterozoic show extremely variable $\Delta^{33}\text{S}$ values (total range of 11.5‰). Post-2.3 Ga old sediments do not show a non mass-dependent sulphur isotope signal.

In addition to the temporal change in $\Delta^{33}\text{S}$, distinct temporal differences also exist considering relationships between $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ as well as between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$. This suggests variations in the respective photochemical reactions (e.g., different sulphur-bearing compounds involved) and/or reflect differences in atmospheric composition with respect to effective UV-shielding. However, we clearly rule out transient oxygen abundances as possible cause. Instead, potential alternatives include variations in the atmospheric abundance of methane and/or in the ratio of carbon dioxide to methane.

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Molecular characterization of Selenium in the environment

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Selenium in the environment is an important element for ecosystem nutrition, but also can be toxic when present at slightly elevated concentrations. Selenium has similar chemistry as sulfur, and thus has multiple oxidation states and molecular forms in the environment. Availability of selenium for uptake by organisms or leaching to ground and surface waters is a function of its speciation. Thus understanding Se speciation and biogeochemistry in the environment is critical for evaluating risks and developing best management practices.

In this presentation results on speciation of Se in rocks, soils, plants, and stream waters located in an active mining region in southeastern Idaho will be presented. Phosphorus ore in the region comprises the Western Phosphate Resource Area. The affected samples have elevated concentrations of Se relative to background levels, resulting from distribution of an ore interbed-shale (middle-waste shale) throughout the surficial environment during mine-site reclamation.

Speciation of Se in the samples was investigated using microscopically focused X-ray absorption spectroscopy. This technique utilizes focused synchrotron-generated radiation to excite core electrons in Se atoms within a sample, and fluorescence or transmission can be monitored either spatially or as a function of impinging energy. It is ideally suited for speciation in natural samples because it is element specific, and has a resolution of a few microns, thus allowing for speciation in heterogeneous samples to be investigated.

In the middle-waste shale, Se existed as reduced Se(0) or Se(II-) species. Three end-members were identified in the shale: Se-substituted pyrite, an iron selenide mineral, and an organic Se phase. Within the soil, both reduced and oxidized Se phases were detected, with the oxidized phases primarily Se(IV) (selenite); very little Se(VI) (selenate) was detected. In the plant materials both reduced organic Se and Se(VI) were identified. Finally, in the stream sediments, reduced Se, and selenite and selenate were identified.

Using the speciation information together with known ecological and biogeochemical processes, we are developing a better understanding of reaction processes, sources, and sinks for Se in the Western Phosphate Resource Area. This detailed information will facilitate a better understanding of the biogeochemical cycling in the system.

Origin of sulfur rich apatite in silicic, calc-alkaline magmas

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We have investigated volcanic apatite from a well-known center of calc-alkaline magmatism – the Oligocene Central San Juan Caldera Complex (CSJCC), Colorado, USA – to constrain the origin of sulfur rich (> ~0.6 wt.% SO₃) apatite found in dacitic to rhyolitic, calc-alkaline magmas. All apatites are small (typically 20-100 µm) and apatite from most units investigated (Fish Canyon Tuff, tuffs and lavas of the San Luis caldera complex) yield SO₃ contents ranging from ≤0.2 wt.% to values of 0.8–2.0 wt.%; the bulk of apatite, however, indicate SO₃ contents of 0.3–0.5 wt.%.

We performed laser-ablation ICP-MS analyses on apatite with a range in sulfur concentrations from selected units to correlate variations observed in sulfur with variations in trace elements (e.g REE) to find evidence for melt compositional changes during crystallization of S-rich vs. S-poor apatites. Apatite among units indicates characteristic compositional changes but within single units, apatite tends to form tight compositional clusters in parameters like Eu/Eu*, La/Yb and Sr contents, while REE concentrations may vary by a factor of two. Exceptions are a few distinct apatites. REE concentrations are typically ≥50–60x of bulk rock and/or of interstitial glass in keeping with other natural systems (e.g. Dempster *et al.*, 2003) and suggest partition coefficients several times the ones of experimental studies.

To constrain actual melt composition from which apatites grew, we find the combination of REE, Sr concentrations and Eu/Eu* most useful. Based on the trend of decreasing Sr towards more silicic compositions of bulk rock & glass for the CSJCC (this study and Lipman, 2004) and a D_{Sr} ≥ 3, all apatite grew from melts more silicic than ~68 wt.% SiO₂ at the exclusion of the most evolved melt composition (~6 ppm Sr, 77 wt.% SiO₂) that is too depleted in Eu to yield a D_{Eu} consistent with those of neighboring REE.

Our study suggests that apatite with low to high S concentrations grew in rhyodacitic/rhyolitic melt requiring either 100's of ppm of sulfur in the melt or alternative mechanisms to explain upper end of S range in apatite. One such alternative explanation may involve some sort of interaction of S-rich fluids (which could be largely derived from an underplated, degassing mafic magma) with crystallizing apatite.

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Climate change in the southern central Andes at 8 Ma

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Being situated in a subtropical high-pressure region with atmospheric subsidence and cold upwelling along the western coast of the continent, the southern central Andes are extremely arid between about 15°S and 27°S. About 20mm/yr rainfall and low erosion rates characterize the Atacama Desert on the western flank of the orogen. With hyper-aridity in this region and less than 200mm/yr rainfall on the adjacent intra-Andean Puna-Altiplano plateau and in the intermontane basins E of the Puna, the southern central Andes thus comprise the most arid sector of the orogen. Despite this inherently arid character, the eastern flanks of the ranges intercept moisture-laden, easterly winds that result in up to 3000mm/yr precipitation. The cause and the timing for the establishment of this pronounced asymmetry is not known, however. Here, we report on stable C-isotope data obtained from paleosols developed in foreland-basin strata of S Bolivia that serve as proxies for paleoclimatic conditions along the eastern flanks of the Andes. Tephra in these sediments provide the chronostratigraphy for the paleoenvironmental evolution. In two sections our preliminary data show $\delta^{13}\text{C}$ values that both decrease from -7 to -8‰ to -11 and -13‰ between about 12.5 and 8 Ma, before they become less negative with an average of -10‰ in the remainder of the profiles. The relatively rapid ~4‰ change in $\delta^{13}\text{C}$ is attributed to a greater availability of moisture and increased climatic variability in this inherently dry area of the Andes. Our data suggest that the landscape was characterized by a mixed C3/C4 vegetation cover since approximately 8 Ma. Moisture availability must have been similar to the present humid conditions with a dry winter season. Holocene $\delta^{13}\text{C}$ values are between -9 and -10‰, thus indicating the dominance of a moisture stressed C3/C4 vegetative cover. Thus, present-day atmospheric circulation patterns and the distribution of rainfall are similar to the conditions during late Miocene time. Based on these observations we suggest that precipitation in the southern central Andes was associated with the South American Monsoon and increased at about 8 Ma. We suggest that enhanced precipitation in this region was closely linked to uplift of the Puna-Altiplano and its adjacent eastern orographic barriers that forced the southward displacement of easterly moisture-bearing winds via the Low Level Andean Jet.

Gabbroic bodies in the Trinity Ophiolite

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The Trinity Ophiolite (N. California) displays discrete silurian to devonian gabbroic bodies hosted by mantle rocks. It might be a good on-land analogue to test the applicability of current accretionary models for slow spreading systems. We report here first results from a mapping campaign in a northern (China Mtn.), central (Bear Creek) and southern gabbroic body (Bonanza King). The central body contains the most regular vertical lithological sequence: mantle peridotite; a shallow dipping transition zone with thick pyroxenitic layers; foliated gabbro; vary-textured gabbro. The northern body displays a disrupted transition zone separated from vary-textured gabbro by plastically deformed amphibolized gabbro. The strain is potentially related to extensional ridge tectonics. The southern body exhibits small exposures of wehrlitic and pyroxenitic rocks overlying mantle peridotite; gabbro and gabbronorite with a mineral foliation subparallel to the local dykes; vary-textured gabbro; doleritic dikes and sills. Two kinds of lateral contacts are observed. (1) Xenolithic margins, described by Cannat *et al.* (1991), demonstrating brittle behavior during emplacement into a cold lithosphere. (2) Dyke-like pyroxenites intruded between mantle peridotite and gabbro. No magmatic strain is obvious. We interpret this as a reactivated contact because of the sharp, sheet-like marginal zone. An inhomogeneous succession of rare peridotite; pyroxenite; doleritic dykes and vary-textured gabbro occurs at the topographic highest parts of two bodies and might represent a roof position. The disrupted character of the transition zones in the northern and southern body suggests the presence of multiple intrusive events which probably caused displacement of existing rock units. Specifically, it is our impression that the abundance of pyroxenites and primitive gabbros is too low relative to the exposed volume of evolved gabbro if a regular, mantle-derived magma is assumed.

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Helium and neon isotopes as mantle tracers

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Noble gas isotopes, especially He isotopes, are widely used tracers for the formation and evolution of the Earth's mantle and atmosphere. Basic concepts on mantle structure and evolution are primarily based on the interpretation of mantle ³He as reflecting primordial, undegassed mantle material. In general, the relative enrichment of ³He observed in MORBs and OIBs, compared to atmospheric values, is interpreted in terms of the retention of primordial He by the mantle throughout the history of the Earth. Primordial He isotopic ratios in terrestrial matter are largely thought to be solar-like, with the deviation from those solar-like ratios increasing during Earth's history caused by the production of radiogenic ⁴He. Thus high ³He/⁴He ratios are interpreted to represent deep mantle material, whereas ratios around 8 R_A (R_A stands for the atmospheric ³He/⁴He ratio of 1.39 × 10⁻⁶) are thought to be representative for the upper mantle. Based on He, Ne and Ar fusion data of fresh, submarine volcanic glasses of a number of Mid-Atlantic Ridge off-axis seamounts we show that melt formation and evolution can have a larger impact on He than on e.g. Ne resulting in a decoupled behavior of He from other elements, such as e.g. Ne or Pb. All obtained He data are indistinguishable from the MORB range. In contrast, Ne isotopic compositions are much more primitive than MORB. Combined He, Ne and Ar systematics show that the source region of these seamounts experienced a preferential loss of He compared to Ne and Ar. This He loss, combined with subsequent ⁴He production, resulted in the decoupling of the He isotope systematics from Ne and Pb. Thus, among He and Ne only Ne has preserved the evidence that a primitive mantle component contributed to the formation of the investigated seamounts. As these seamounts are not fed from a mantle plume being derived from the deep mantle, the primitive Ne component resides within the upper mantle, implying that primitive noble gases are not necessarily indicative for deep mantle material. Our studies point out the necessity of obtaining Ne data in addition to He for the modeling of mantle formation and evolution and correct source characterization.

He-Ne-Ar isotope constraints on the nature and origin of high ³He/⁴He mantle

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Olivine phenocrysts from early Tertiary picrites from Baffin Island (BI) and West Greenland have ³He/⁴He = 38-50 R_a (*n*=24). The high ³He/⁴He are consistent with derivation from a mantle reservoir that is relatively undegassed compared to the depleted upper (MORB-source) mantle. Although Ne and Ar concentrations are typically 2 orders of magnitude lower than in basaltic glasses a low blank crusher is allowing Ne and Ar isotope determinations of high-³He/⁴He olivines. On a conventional 3-isotope plot, the BI picrites are indistinguishable from the Iceland and solar trends; the highest ²⁰Ne/²²Ne is 11.3. ⁴⁰Ar/³⁶Ar are typically less than 1,000. ³⁸Ar/³⁶Ar are indistinguishable from air values providing no evidence for solar Ar in the high-³He/⁴He mantle. Most samples define a trend in ²⁰Ne/²²Ne-⁴⁰Ar/³⁶Ar space that is consistent with mantle end-member with ⁴⁰Ar/³⁶Ar of 6,000-8,000. ⁴He*/²¹Ne* and air-corrected ³He/²²Ne imply the magmatic noble gases have suffered intense fractionation. This is supported by co-variation of ⁴He*/⁴⁰Ar* and ³He/³⁶Ar. The elemental fractionation is consistent with recent magmatic degassing and provides no evidence for an ancient degassing event necessary if the high-³He/⁴He mantle was a residue of early Earth depletion. The BI picrites plot on a trend in ⁴He*/²¹Ne*-³He/²²Ne space defined by basaltic glasses from Iceland. This is distinct from samples of Kola intrusives and we tentatively propose different degassing/depletion histories for the high-³He/⁴He mantle domains.

Structural incorporation of Eu(III) into calcite: Process understanding on a molecular level

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Demonstrating the geochemical aspects of the long term safety of a nuclear waste repository can significantly be improved by a molecular level understanding of the actinides behavior in the geosphere. In particular the interaction of radionuclides with minerals (adsorption, structural incorporation) strongly affects their mobility and retardation. In this presentation we will focus on the interaction of trivalent actinides and lanthanides with calcite, with special focus on the structural incorporation.

Calcite (CaCO_3) is an omnipresent mineral in many rocks which are discussed as potential host for a nuclear waste repository. Furthermore, many waste repository designs include cement based components. Calcite is one of the major secondary alteration products formed during the degradation of cement over geological timescales. Actinide and lanthanide partition data derived from co-precipitation experiments indicate a high sorption affinity of these elements to calcite but a comprehensive understanding of actinide and REE uptake by calcite is not yet available. From a geochemical perspective the molecular level substitution mechanism is of key interest. Trivalent actinides and lanthanides have a similar ionic radius compared to Ca, the charge compensation mechanism upon substitution is unclear despite various recent studies. We have studied synthetically doped calcite crystals with Time Resolved Laser Fluorescence Spectroscopy and Extended X-Ray Absorption Fine Structure Spectroscopy. The focus has primarily been on Eu(III), due to its fluorescence properties. The structural parameters of Am(III) doped calcites obtained by EXAFS confirm the substitution of Ca^{2+} within the calcite structure. Site-selective TRLFS measurements at temperatures < 20 K show the presence of various incorporated molecular species. The incorporation into calcite involves several structurally distinguishable "sites". These sites may be due to local lattice distortions/relaxations around the metal ion in the calcite structure. These investigations give a mechanistic understanding of the incorporation process and show that the incorporation of trivalent metal ions is not a simple coupled substitution mechanism but involves complex substitution mechanisms.

Bugs in stress: Microbial control of surface reactivity in a stress field

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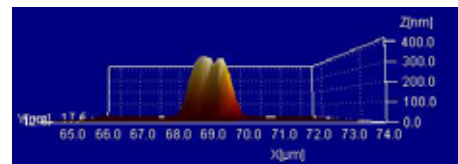
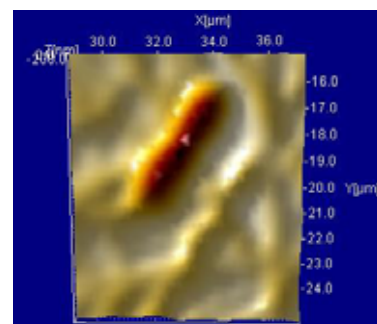
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The reactivity of a solid surface is strongly affected by the imposition of non-hydrostatic stress: the resulting strain rate is a driving force for mass transfer during pressure solution. Previous work [1,2] has shown that bacteria (e.g., *Shewanella oneidensis* MR-1) recognize and modify crystal surfaces through apparent recognition of surface energy, and are thus potentially sensitive to the distribution of surface stress as well. Here we present the results of a novel integration of vertical scanning interferometry (VSI) with the means to control and measure stress distribution on a solid surface, through controlled deflection of a cantilever beam. These deflection data, measured with VSI at (sub-)nanometer vertical and sub-micron lateral resolution, yield a high resolution map of surface deformation. These data can be compared with Euler-Bernoulli beam bending theory and elastic constants to yield a quantitative prediction of material response. This controlled system can be immersed in a fluid cell inoculated with MR-1 (or other microorganisms) and thus permits the study of bacterial interaction with a stressed surface.

This new technique can be used for abiotic systems as well and has a large potential for applications in earth, environmental, and material sciences.



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Duration of metamorphism in the eclogite type locality

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The eclogite type locality is located in the Kor- and Saualpe region of the Eastern European Alps. The region also hosts one of the largest shear zones of the orogen: The Plattengneiss shear zone. Peak metamorphism occurred around 15 kbar and 700°C and the duration of its metamorphic cycle is loosely constrained by peak ages around 80 Ma and fission track ages around 50 Ma.

Despite the high temperatures of peak metamorphism, equilibration of both, major elements and radiogenic isotopes is extremely heterogeneous so that metamorphic conditions and the absolute timing thereof are not very well constrained. The lack of pervasive equilibration suggests that the highest grade metamorphic conditions were only achieved for a very short time and/or at very dry conditions.

In a series of projects over the last 10 years we have attempted to constrain both, the water content of the rocks and the time scales of metamorphism using petrological rather than geochronological methods. Although we generally obtain very short time scales and dry conditions, our studies are plagued by the inherent problems of petrological methods.

Nevertheless, on the largest scale, we have determined a metamorphic field gradient from north to south across the Koralpe range that shows that metamorphic conditions increase by less than 20°C per kilobar. We suggest that this shallow field gradient may be interpreted in terms of a non-lithostatic pressure gradient. This in turn implies that these conditions prevailed only very briefly.

Fractional crystallization of monosulfide solid solution from sulfide liquids lead to the PGE enrichment in the Jinchuan Ni-Cu sulfide deposit, western China

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Discordant lenses of Pt-Pd enriched zones (ores bearing up to 1.0 ppm of Pt or Pd) have recently been identified in the sulfide-bearing peridotite of the Jinchuan Cu-Ni-PGE (Platinum group element) sulfide deposit, China. Chalcopyrite, pyrrhotite, and pentlandite occur in both Pt-Pd enriched zones and normal ores, but Cu-bearing minerals such as cubanite and Bi-, Te-, and As-bearing minerals are more abundant in the Pt-Pd enriched zones. Sperrylite is the major Pt-host minerals in the Pt-Pd enriched zones interstitially and occurs mainly as euhedral grains within base-metal sulfides which occur among the cumulates of olivine. PGE-enrichment is found only in sulfide-bearing samples. In orebody # 1 and orebody 24, Rh, Ru, and Ir are positively correlated, but a negative Ir-Pd and Ir-Pt correlation. However in orebody 2 Rh, Ru, Pt, Pd and Ir are positively correlated.

Taken together, the elemental correlations and mineralogical data support a model for the origin of Pt-Pd rich ores in Orebody 1 and Orebody 24 of the Jinchuan deposit are consistent with fractional crystallization of monosulfide solid solution from sulfide liquids on cooling; The origin of Orebody 2 involves variable magma/sulfide liquid mass ratios (R-factors).

New $^{40}\text{Ar}/^{39}\text{Ar}$ and K-Ar ages from Macolod Corridor, SW Luzon, Philippines: Implication for its volcanic history

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Macolod Corridor, southwestern Luzon, Philippines, is an extensive Quaternary volcanic field including Taal caldera and many monogenetic/polygenetic volcanoes. Recently reported K-Ar or ^{14}C ages (Listanco, 1994; Sudo *et al.*, 2000) suggest that several volcanoes have younger ages than e.g., 0.14 Ma.

However, the history of the possible caldera, located at the central lobe of the lake Laguna de Bay, at the north of Macolod Corridor has not been well understood. Radiometric dates remain few other than the K-Ar age, 1.84 ± 0.07 Ma (error: 1σ), from an essential scoria (sample name 013006; Sudo *et al.*, 2000) with a size of ~30 cm in the pyroclastic (scoria) flow at the northeastern rim, or the ^{14}C ages of 5000 to 47000 yBP, from pyroclastic materials between Laguna de Bay and Metropolitan Manila.

In this study, the essential scoria (sample name P4-2), smaller than 10 cm, included in the pyroclastic (scoria) flow near Teresa city located at the north of Laguna de Bay, and the scoria, 013006, have been dated at the new $^{40}\text{Ar}/^{39}\text{Ar}$ chronology laboratory in the University of Potsdam. The system used consists of a continuous CO_2 laser, Micromass 5400 noble gas mass spectrometer and the ultra-high vacuum tubes adopting SAES getters and a cold trap. The prepared samples were irradiated for 96 hours at the reactor in the Geesthacht Neutron Facility (fast neutron flux: 1×10^{12} n/cm²/s) together with the Fish Canyon Tuff sanidine and crystals of CaF_2 and K_2SO_4 .

The obtained $^{40}\text{Ar}/^{39}\text{Ar}$ plateau ages are 1.85 ± 0.01 Ma and 1.83 ± 0.02 Ma from P4-2, while 1.92 ± 0.03 Ma from 013006. With the K-Ar age, 1.82 ± 0.05 Ma (unpublished), obtained from the scoria in the same outcrop for 013006, all the ages show agreement within 2 sigma error. These ages would be the constraints for solving the history of the caldera at Laguna de Bay.

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Gabbros drilled by IODP Leg 305, 30°N, Mid-Atlantic Ridge

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IODP Hole 1309D (Legs 304/305) penetrated 1415 m into the core-complex of the Atlantis Massif at 30°N, Mid-Atlantic Ridge. Of the 75% recovered rock, 96% is gabbroic. Possibly, a larger-scale magmatic cycle is preserved between 600 und 1240 mbsf, as marked by olivine-rich troctolites at the base and more common gabbro-norites near the top. In detail, however, internal magmatic contacts are numerous with more evolved rocks intruding into less evolved ones. Here we present an overview of the 800-1200 mbsf interval and a detailed study of the transition from evolved rocks below 1235 mbsf to overlying primitive gabbros.

Geochemically, there is a good correlation between the REE in cpx, the Mg# in cpx, and lithological evolution. The data can be modeled as increments of batch fractionation ranging from 5 to >80% from a primitive N-MORB. There is no immediate need for magma replenishment. The rims of nearly all clinopyroxenes were overprinted by an evolved melt. A three stage model is required to explain the data set: (1) a cumulus phase; (2) displacement of residual melt and formation of new cumulate bodies from it. These two processes can explain the presence of well-equilibrated, but differently evolved cores of clinopyroxene. (3) Compaction of residual melt and differentiation of it as it migrates through the cumulus pile. This stage explains the late overprint of the clinopyroxene rims.

'Green' geosequestration: Secure carbon sequestration via plant silica biomineralisation

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Phytoliths form via biomineralization processes as microscopic grains of silica in plants, especially grasses. During plant growth a proportion of the organic carbon produced by plants is encapsulated by silica within the microscopic phytoliths. This phytolith occluded carbon (PhytOC) usually comprises much less than 1% of the dry weight of plants, and less than 10% of the total carbon pool in grassland topsoils (with ages of < 200 years). However, data from soil chronosequences shows that the high resistance of the PhytOC fraction (relative to the other soil carbon fractions) against decomposition processes results in PhytOC comprising ~70% of the total carbon pool in grassland topsoils that have been isolated for >3,000 years from fresh plant material addition by burial. Therefore, unlike most plant matter, which readily decomposes returning CO₂ to the atmosphere, the organic carbon occluded in phytoliths effectively sequesters carbon in soils and sediments in a very secure manner. This 'green' geosequestration process (i.e. occlusion of carbon in phytoliths) is currently responsible for the secure sequestering within soil of ~300 million tonnes of CO₂ equivalent per year globally.

More over different plant types biomineralise silica and yield PhytOC at greatly different rates. Some major crops produce over 100 times more PhytOC than other major crop types. Furthermore, varieties within a single major crop type, such as sugar-cane and sorghum, have been found to produce widely differing quantities of PhytOC. This suggests that crop/cultivar choice decisions by farmers and foresters etc have a considerable impact on the amount of soil carbon sequestered and are a significant contributing factor affecting the global carbon cycle. It follows that the management of PhytOC in crops, pastures, forests etc has the potential to greatly enhance the current rates of secure terrestrial carbon sequestration.

Subducted noble gas and halogen preserved in wedge mantle peridotite from the Sanbagawa belt, SW Japan

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Water-rich fluids released from subducting slabs play an important role in arc volcanism. Indeed, subduction volcanism is thought to efficiently return volatiles contained in subducting material back to the Earth's surface. Less than 100% removal of the volatile component may result in volatile recycling into the deep mantle [1]. The volatile composition of subducting fluids is however, not well characterised. The Higashi-akaishi peridotite body in the Sanbagawa metamorphic belt, southwest Japan, is possibly a unique example of a km-scale sliver of a former mantle wedge exhumed from depths of at least 100 km. Serpentine dominated micro-inclusions in olivine grains in the peridotite are regarded as relics of former water-rich inclusions developed in the wedge mantle above a subducting slab. Thus, it is expected that these micro-inclusions should preserve characteristics of slab-derived fluids. Determination of their compositions could provide important geochemical constraints on subduction zone processes.

Noble gas and halogen determination of the micro-inclusions has been carried out using noble gas isotope analysis of both neutron-irradiated and unirradiated samples. The following isotopic characteristics have been determined: (1) ³He/⁴He ratios of 1.4-1.8 Ra represent a mixture of mantle and radiogenic He; (2) ⁴⁰Ar/³⁶Ar ratios up to 470 are close to the atmospheric ratio with a small contribution of mantle and/or radiogenic Ar; (3) Seawater-like noble gas elemental ratios enriched in heavy noble gases; and (4) halogen (Cl, Br, and I) composition is similar to marine pore fluids and brines. These characteristics imply that noble gases and halogens with compositions little different to marine pore fluids are injected into the mantle wedge just above the subducting slab.

The subducted halogen and noble gas elemental ratios are clearly distinct from those of arc volcanic gases. This implies that the Higashi-akaishi peridotite body has frozen in and preserved an inferred but previously unseen part of the volatile recycling process. Return of these volatiles to the atmosphere via arc volcanism requires the addition of a mantle component and fractionation during degassing. A small proportion preserved in the downgoing slab can explain the heavy noble gases observed in the convecting mantle.

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Using reflectance spectroscopy for the reconstruction of penguin palaeoecological process in Antarctic ornithogenic sediments

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The present study explored the application of the rapid, cost-effective, non-destructive and simultaneous technique of reflectance spectroscopy within visible-near-infrared region to infer penguin palaeoecological records in the maritime Antarctic. A total of 106 samples taken from four sediment cores (Y2, Y2-4, Y4, AD3) on the Ardley Island were measured by both chemical and spectral methods. These cores were previously reported to be influenced by penguin guano, and nine elements including sulfur (S), phosphorus (as P₂O₅), calcium (as CaO), copper (Cu), zinc (Zn), selenium (Se), strontium (Sr), barium (Ba), and fluorine (F) were identified as bio-elements; their concentrations could be used as inorganic geochemical indicators for tracking historical penguin population change. The reflectance (r) and its derived indexes were employed to develop calibrations for predicting nine bio-element concentrations, using stepwise multiple linear regression (s-MLR) and principal component regression (PCR) approaches. R between optimal spectra-predicted and chemically analyzed concentrations were Ba: 0.894, all the other eight elements >0.954 for s-MLR; Ba: 0.926, all the other eight elements >0.963 for PCR.

Furthermore, principal component analysis (PCA) was performed on all the reflectance spectra data and the results showed that the first two factors were able to account for 98.9% of the variance of the data. The first PCA factor(PC1), accounting for 95.8% of the total variance, could be explained to bear the information of the content of penguin guano, and thus the PC1 score against depth of the samples (curve A) indicated the fluctuation of historical penguin population. In addition, by using spectra of pure guano and pure soil, these absorbance spectra data (log1/r) of ornithogenic sediments were linearly separated to guano part and soil part. The penguin population change inferred from the separated guano proportion (curve B) was consistent with curve A, and both curves showed similar historical change trends as inferences from inorganic elements and isotopes. Overall, this study demonstrated that using reflectance spectroscopy to infer palaeoecological information recorded in Antarctic ornithogenic sediments is feasible.

Acknowledgment

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The coupling between plate subduction and intraplate evolution in eastern China

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Plate interactions along subduction zones usually cause deformations of overlaying crusts as shown in the Andes. Numerical modelling shows that plate interaction during plate subduction is of critical importance for intraplate tectonic evolutions of the American continent [1].

Eastern China was an active continental margin related to the subduction of the paleo-Pacific plate under Eurasia from Jurassic to Cretaceous. This continent is well known for the removal of subcontinental lithosphere mantle with complicated geological evolutions, which leads to different models, ranging from extension to subduction-related compression and crust delamination etc. We find that the Cretaceous tectonic evolution in eastern China matches remarkably well with the drifting history of the paleo-Pacific plate. The most pronounced phenomenon is that the eastern China large-scale orogenic lode gold mineralisation occurred at about 125 Ma [2], concurrent with the major shift in the drifting direction of the subducting paleo-Pacific Plate [3] and the formation of the Ontong Java Plateau. Given lode gold deposits usually formed onset of compressional or transpressional deformations, the lode gold deposits dated the major tectonic change from extension to transpression in eastern China [4], consistent with the subduction regime and other geological records in the region. The Early Cretaceous drifting history of the paleo-Pacific also matches with other tectonic and magmatic evolutions in eastern China, suggesting that the major geological events in eastern China in the Early Cretaceous have been mainly controlled by the subduction of the paleo-Pacific plate, and that plate interactions are important driving forces for intraplate tectonic evolution in general. This provides a new angle of view to understand the tectonic evolution of the eastern Euroasian continents, e.g., the mechanism behind lithosphere thinning in eastern China as well as the evolution of the Tan-Lu Fault.

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$^{40}\text{Ar}/^{39}\text{Ar}$ dating of muscovite from the Maofeng Granite, N-Guangdong Province, China

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The Maofeng Granite, located in the Guidong granite composite, N-Guangdong Province, China, has been paid much attention to by geoscientists because of its hosting several big uranium deposits. Two muscovite concentrates have been prepared from representative samples collected from the outcrop of the granite body. They were analysed using incremental-release $^{40}\text{Ar}/^{39}\text{Ar}$ method. The $^{40}\text{Ar}/^{39}\text{Ar}$ apparent ages of the two samples are shown in Fig. 1.

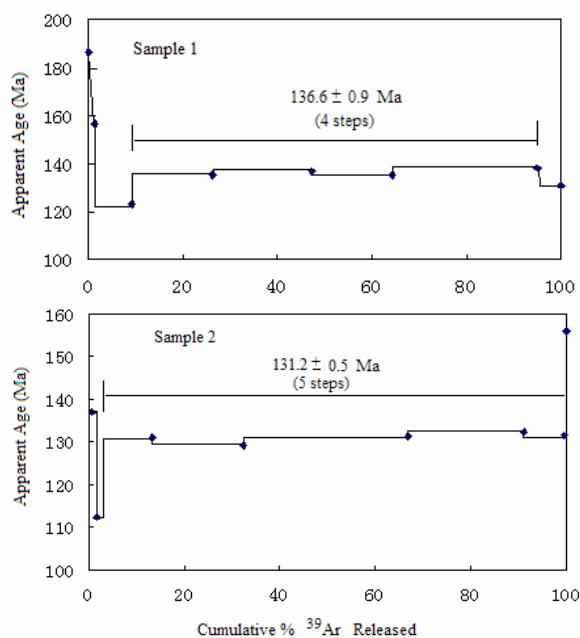


Figure 1. $^{40}\text{Ar}/^{39}\text{Ar}$ apparent ages of muscovite concentrates from the Maofeng Granite. Plateau ages are listed on each spectrum.

The plateau ages ranging from 131.2 ± 0.5 to 136 ± 0.9 Ma are much different from the single grain zircon U-Pb ages varying from 207.6 ± 3.2 to 219.6 ± 0.9 Ma of the Maofeng Granite reported by previous researchers. In the area, one of the major uranium mineralization periods was dated back to 122 to 138 Ma ago. These evidences suggest that the muscovite was formed from the hydrothermal fluid which resulted in uranium mineralization, and that the plateau ages did not reflect the age of the Maofeng granite itself but the age of the U ore-forming hydrothermal activity.

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Oxygen isotopic zonality at the Iultin Sn-W Deposit (Chukotka, North-East of Russia)

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The oxygen isotope composition of host rocks and main vein minerals was studied at the large well known Sn-W Iultin deposit with application to the role of mixing fluids of different origins in the deposition of Sn-W ores in granite-related hydrothermal systems.

The deposit is located in the exo- and endocontact of leucogranite stock (K_2) and is formed by the series of the proximate quartz veins in hornfelsized sandstone-schist rocks (T_{1-2}). The veins and greisens are largely composed of the productive mineral assemblage (quartz, muscovite, cassiterite, wolframite, arsenopyrite, subordinate beryl, scheelite), formed from sodium chloride boiling solutions enriched in CO_2 and CH_4 at T 270-350°C, P 0,5-1,0 kbar as it followed from fluid inclusion data. The postore sulfide and fluorite-carbonate assemblages are poorly developed.

The oxygen isotope composition of the rocks was examined in: a) metamorphosed sedimentary rocks of outer part of hydrothermal system, b) the contact part of the leucogranite cupola, c) the altered wall rocks in the central part of the deposit across the large ore body (62/50) and d) the wall rocks of the veins (7,10), poor in Sn-W ores. It was found that large (hundred meters) low- ^{18}O zones have been formed in the central part of the Iultin hydrothermal system. The $\delta^{18}\text{O}$ values decreased monotonously from the initial 12‰ (1km from the contact) to 3-5‰ at the contact with granite. Substantial ^{18}O decrease in the contact zone, formed by greisenized granites, is the result of active movement of hydrothermal solutions and is explained by higher permeability in comparison with metamorphosed sedimentary rocks (Spasennykh *et al.*, 2002). During the development of vein ore bodies the wall rocks were altered insignificantly in oxygen isotope composition. The high $\delta^{18}\text{O}$ values of minerals of productive association bore witness to magmatogenic source of the fluids. The notable depletion of the wall rocks in ^{18}O took place during the final stage, when meteoric waters dominated in the hydrothermal system. That time no significant ascending fluid flows were focused within the veins. The initial picture of oxygen isotope zonality, connected with ore deposition, had been wiped away by active interaction of exogenic waters with host rocks.

This study was supported by the Russian Foundation for Basic Research (project nos. 03-05-65036, 07-05-00432)

Synchrotron-based studies of fluids, mineral-water interfaces and glasses

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Synchrotron-based analytical methods have proved to be valuable in a wide variety of studies of fluids, glasses and mineral-water interfaces. This presentation is an overview of experiments of this nature being conducted at the GSECARS facility at the Advanced Photon Source (USA).

X-ray absorption fine structure (XAFS) spectroscopy is one of the principal methods used in these studies. One such microbeam application involves the determination of valence states for multivalent elements in igneous glasses, which in turn are used as proxies for oxygen fugacity inferences for both terrestrial and extraterrestrial magmas (e.g., Sutton *et al.* 2005). MicroXAFS is also used in ore-relevant studies to establish the speciation of metals in hydrothermal fluids. These applications involve measurements on fluid inclusions (both natural and synthetic) where the samples are analyzed in situ above their homogenization temperature using a heating stage (e.g., Berry *et al.* 2006).

Mineral-water interface studies aim to establish the atomic-scale structures of mineral surfaces, the structural and reactivity changes that occur during hydration and the resultant metal sorption properties of these surfaces. These in situ experiments typically involve combinations of x-ray reflectivity, crystal truncation rod, x-ray standing waves and grazing-incidence XAFS methods. A focus of this work is the determination of structural and reactivity changes of hydrated metal oxide surfaces (e.g., Eng *et al.* 2000).

Fluids can be imaged within objects using x-ray computed microtomography (CMT). One aspect involves the determination of the distribution and flow properties of multiphase fluids in soil columns (e.g., Culligan *et al.* 2006). CMT methods can also reveal transport paths of metals in plants (e.g., McNear *et al.* 2005).

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Raman spectroscopy of organics in Antarctic micrometeorites

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Introduction

Micrometeorites are expected to be the major source of the C flux from extraterrestrial materials delivered to the earth and might represent a major contribution to the pre-biotic organic matter on the early earth (Maurette 2006). On the other hand, organics from carbobaceous chondrites have been characterized non-destructively by means of Raman microspectroscopies (Raynal, 2003; Matrajt *et al.*, 2004).

Methods

Raman spectra have been measured on 73 points of 11 unmelted Antarctic micrometeorite (AMM) grains pressed on aluminum foils under a Raman microscope. Peak positions, full widths at half maximum (FWHM), band intensity ratios (I_D/I_G) and band area ratios ($A_D/A_{(D+G)}$ (%)) for D (defect: ~ 1360 cm^{-1}) and G (graphite: ~ 1600 cm^{-1}) bands were determined for the AMMs and compared with the literature data on carbonaceous chondrites and other cosmic materials.

Results and Discussion

The peak position and FWHM of G band of the AMMs are ranging from 1581 to 1593 cm^{-1} and from 87 to 133 cm^{-1} , respectively. These value ranges are almost the same as those for CM2 carbonaceous chondrites. The peak position and FWHM of D band for the AMMs are from 1357 to 1379 cm^{-1} and from 166 to 271 cm^{-1} , respectively. This region for the AMMs mostly overlaps with the region for CI1s. The D peak position range of the AMMs is similar to those for CM2 and CR2 chondrites. The I_D/I_G and $A_D/A_{(D+G)}$ (%) are ranging from 1.1 to 1.7 and from 65 to 78, respectively. These distributions of the AMMs are close to Orgueil carbonaceous chondrite (CI1). $A_D/A_{(D+G)}$ band area ratios (%) of the AMMs are in the similar range to those for CR2 and Tagish Lake carbonaceous chondrites.

These Raman features of macromolecular carbonaceous materials in the AMMs are similar to those in C1 and C2 chondrites. The AMMs studied here might have the aqueous alteration level higher than 2 and have possibly delivered useful organic components to the early earth.

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Osmium behavior in a subduction zone setting elucidated from Cr-spinel sands of boninites and tholeiite in Bonin islands

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Osmium (Os) isotope is a sensitive tracer of crust and sediment as its eroding form, because of significant contrast between a high Os isotope ratio of crust and sediments ($^{187}\text{Os}/^{188}\text{Os} > 0.5$) and a low ratio of mantle ($^{187}\text{Os}/^{188}\text{Os} < 0.13$). Therefore, Os isotope provides information on slab components contribution to the mantle source of island arc lavas (Brandon *et al.*, 1999; Borg *et al.*, 2000; Alves *et al.*, 2002). Radiogenic Os isotopic compositions are commonly found in volcanic lavas and peridotite xenoliths in a subduction zone setting. Though most of the authors had attributed these high $^{187}\text{Os}/^{188}\text{Os}$ to the input of the slab component to the mantle source, some pointed out that assimilation of crustal materials during magma ascent possibly reproduce the elevated Os isotope ratios of the arc lavas (Lassiter and Luhr, 2001; Woodhead and Brauns, 2004). Since then, whether the high Os isotope ratios of arc lavas are caused by contribution of slab component or by assimilation of the overlying crust has long been highly debated.

Here we report the unradiogenic Os isotopic ratios of Cr-spinel sands from Chichi-Jima and Yome-Shima boninites and the significantly high $^{187}\text{Os}/^{188}\text{Os}$ of Cr-spinels of the Mukoojima tholeiite, Izu-Bonin arc. As Cr-spinel is resistant to later alteration and weathering and, more importantly, is the early stage crystal in the fractional crystallization, it preserves the chemical and isotopic compositions of very primitive magma in its melt inclusion and spinel itself without any later stage crustal contamination. Therefore, extremely high $^{187}\text{Os}/^{188}\text{Os}$ of 0.1429 of Mukoojima tholeiite is most likely caused by inputs from slab components, not by assimilation of the overlying crust. Unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ of Cr-spinel of Yome-shima and Chichi-jima boninites (0.1232 and 0.1242, respectively) indicate that Os is not mobile under a boninite formation condition. As a result, we demonstrate that Cr-spinel is the most useful mineral to decode the Os isotopic compositions of primitive arc magmas.

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Reduction of U(VI) by *Shewanella putrefaciens* in the presence of organic acids

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Introduction

The oxidation state of uranium is one of the important factors that affect its migration in the environment. Although microbial reduction of U(VI) has been extensively investigated, limited information is available of the effects of organic acids. We examined the reduction behavior of U(VI) by *Shewanella putrefaciens* in the organic acid solutions.

Experimental

Shewanella putrefaciens was incubated in anoxic medium at pH 7 that contained 1mM UO_2^{2+} , 50 mM lactic acid and 100 mM organic acids (acetic, oxalic, malonic, succinic, adipic, malic, tartaric, citric acid or EDTA). Aliquots of medium were periodically withdrawn, and filtered. Dissolved uranium concentrations and UV-vis spectra of the aliquots were measured. Precipitates generated were analyzed by XANES and SEM. The medium without organic acid (except for lactic acid) was examined as a control.

Results and Discussion

In the control medium and the media containing acetic or adipic acid, dissolved uranium decreased with time, and precipitates were observed. The XANES spectra of the precipitates showed that the precipitates contained U(IV). The SEM analysis showed that the precipitates were uraninite (UO_2). In the other media, dissolved uranium was almost constant. The UV-vis spectra showed that dissolved U(VI) was reduced to U(IV), and it was present as U(IV) organic complex in the medium containing oxalic, tartaric, citric acid or EDTA. No evidence of U(VI) reduction was observed in the media with succinic or malic acid. These results suggest that the reduction behaviors of U(VI) by *S. putrefaciens* are categorized into three cases depending on organic acid.

Provenance and post-sedimentary low-temperature evolution of the James Ross Basin sediments (Antarctic Peninsula) based on zircon and apatite fission-track analysis

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James Ross Basin contains one of the thickest and most complete Jurassic-Paleogene age sedimentary successions anywhere in the Southern Hemisphere. The basin is filled by a sequence of arc-derived clastic and volcanoclastic marine sediments through the Late Jurassic to Late Eocene.

In order to reconstruct thermal history for basin low-temperature evolution of potential sedimentary resources and post-sedimentation successions, we dated detrital zircons and apatites from the sequence of sandstones collected from the James Ross and Seymour Islands using fission-track (FT) thermochronology. All zircon FT ages are older than apatite FT ages provided in the identical individual rocks. Provenance of individual FT zircons and apatites ages varies in wide spread of Carboniferous to Early Paleogene ages between ~60 to ~350 Ma. Jurassic-Cretaceous ages of northwest James Ross Island are probably compatible with derivation of sediment from western lying Mt. Reece and Mt. Bradley region, where the rocks of the Antarctic Peninsula batholith appears.

Sediments from Seymour Island are probably originating from Trinity Peninsula Group and Antarctic Peninsula Volcanic Group. Shortening of tracks was due to subsequent volcanic/magmatic activity before transport of rocks and deposition into the James Ross Basin or alternatively, due to volcanic reheating after deposition.

Time-temperature modelling of the apatite fission-track samples from Seymour Island (Marambio and Seymour Island Groups) shows a similar thermal history style, involving a period of total thermal annealing and subsequent cooling (erosion/denudation). The samples were above 120°C until about the Upper Triassic (220 – 210 Ma) age and then followed by the period of relatively quick Neogene and Quaternary exhumation (since ~30 – 40 Ma) to the present erosion surface.

Isotopic and trace element evidence for groundwater discharge in the coastal zone

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Determination of the relative importance of freshwater discharge from surface and groundwater sources into coastal estuaries and lagoons is important in making assessments regarding water control policies. In this study, variations in δD , $\delta^{18}O$, $\delta^{13}C$, and concentrations of Sr, Ba, and Mg relative to Ca have been used to distinguish the input of fresh groundwater from rainwater and surface discharge into coastal ecosystems of South Florida (Biscayne Bay and Florida Bay). These tracers are able to distinguish between these various sources, because rainwater has relatively negative $\delta^{18}O$ and δD values and low concentrations of cations. Groundwater also has depleted $\delta^{18}O$ and δD , but low Sr/Ca, Mg/Ca, and Ba/Ca ratios. In contrast, surface waters have relatively positive $\delta^{18}O$ and δD values, intermediate concentrations of Ca, high concentrations of Ba, and negative $\delta^{13}C$ values (SWART and PRICE, 2002). The differences in the geochemical parameters arise because (i) surface waters in South Florida are highly evaporated thereby enriching δD and $\delta^{18}O$ values, (ii) surface waters are highly influenced by surface organic activity which produces waters depleted in $\delta^{13}C$ and elevated in Ba, (iii) groundwaters dissolve the local carbonate rocks which contain high concentration of Ca, but relatively low concentrations of Ba, Sr, and Mg; these waters also contain relatively positive $\delta^{13}C$ values. Our results indicate that within Florida Bay, the input of fresh groundwater contributes an insignificant amount to the hydrological balance. Instead the salinity is controlled by runoff and precipitation. In contrast in Biscayne Bay, groundwater, surface water, and direct precipitation all contribute equally to the salinity balance.

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In situ U/Pb geochronology of baddeleyite by LA-ICPMS

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Baddeleyite (ZrO_2) is a useful U-Pb chronometer for determining magmatic crystallization ages of silica-poor rocks that failed to form zircon. In situ baddeleyite dating has been plagued by analytical problems, however, limiting its application. Crystal orientation effects produce unacceptably large variations in $^{206}Pb/^{238}U$ ratios measured by ion microprobe so that ages must be determined from $^{207}Pb/^{206}Pb$ ratios alone. Laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) analyses have produced $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ratios that plot in arrays extending far above concordia, suggesting severe laser-induced Pb/U fractionation. Correction procedures for instrumental mass bias, in particular the extent of matrix effects between baddeleyite and common zircon standard reference materials (SRMs) used for calibration of measured isotope ratios, are poorly defined. We have dated two baddeleyites of known (TIMS) age using a Finnigan ELEMENT-XR magnetic sector ICPMS coupled to a GeoLas 193 nm ArF excimer laser ablation system. The baddeleyites are from carbonatite in the Phalaborwa Complex in South Africa (PHB; 2059.8 ± 0.8 Ma) and gabbroic anorthosite of the Duluth gabbro complex at Forest Center, Minnesota (FC-1; 1099.0 ± 0.6 Ma). Two methods commonly used for LA-ICPMS U-Pb dating were tested. The first involved spot analysis (40 micron beam, 5 Hz, $3 J/cm^2$) and calibration of isotopic ratios by standard-sample-standard bracketing with zircon 91500 as the calibrant. The second employed raster analysis (10 micron beam, 10 Hz, $5 J/cm^2$, making a 40 by 40 micron box pattern) and Pb/U determinations by the "intercept" method. Mass bias corrections are made by reference to a tracer solution of Tl-Bi- ^{233}U - ^{237}Np (with a composition defined by reference to zircon SRMs) aspirated into the argon plasma at the same time as sample ablation. Both spot and raster analyses exhibited laser-induced U/Pb fractionation during analysis, but the degree of fractionation was much more severe for the spot analyses. PHB baddeleyite exhibited much more fractionation than FC-1 baddeleyite. The reason is unclear but may be related to polysynthetic twinning on {100} being less well-developed in FC-1. Pb and U are heterogeneously distributed in the PHB baddeleyite: there is much less scatter on Pb/U ratios when it is drilled perpendicular to the {100} planes than when drilled parallel to them, suggesting that Pb/U ratios are more homogeneous at the scale of laser sampling in this orientation. Both zircon SRM and tracer solution calibration methods produced inadequate mass bias corrections for measured Pb/U and $^{207}Pb/^{206}Pb$ ratios and erroneous ages for analysed baddeleyites. LA-ICPMS U-Pb ages with accuracies comparable to those determined for zircon can be attained using raster analyses, intercept corrections, and a tracer solution calibrated for baddeleyite.

Efficiency of Cl recycling during subduction of oceanic crust: Constraints from melt inclusions in HIMU lavas

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The amount of chlorine that is recycled into the deep mantle through subduction processes is poorly constrained. Estimates of the chlorine content in recycled, dehydrated oceanic crust range from <50 ppm [1] up to ~200 ppm [2,3].

In order to better constrain the Cl content in subducted crust, we have examined Cl concentrations as well as Cl/K₂O and Cl/Nb ratios in olivine-hosted melt inclusions in HIMU lavas from the island of Raivavae, Austral Islands. Raivavae lavas span a wide range of lead isotopic values, with $^{206}Pb/^{204}Pb$ ranging from ~19.3 to 21.3. Previous isotopic and trace element studies suggest that Raivavae lavas derive from a mantle source containing ancient dehydrated oceanic crust.

Chlorine and K₂O concentrations range from 40-1070 ppm and 0.22-3.5 wt.% respectively. The majority of Cl/K₂O ratios range from 0.01-0.12 and Cl/Nb ratios range from 5-25. Cl/K₂O and Cl/Nb ratios are positively correlated with $^{206}Pb/^{204}Pb$ and negatively correlated with $^{207}Pb/^{206}Pb$. In addition, a positive correlation exists between Cl/K₂O and Nb/Zr. No correlation exists between host olivine forsterite content and Cl concentration or Cl/K₂O ratios.

The lack of correlation between host forsterite content and inclusion Cl/K₂O and the correlation between Cl/K₂O and Pb-isotopes suggest that Cl contents and Cl/K₂O ratios in HIMU lavas are not controlled by shallow assimilation processes. This contradicts the previous suggestion of [1], who argued that elevated Cl/K₂O ratios in some Raivavae lavas resulted from assimilation of Cl-rich brine. Instead, the high Cl/Nb and Cl/K₂O ratios observed in the HIMU samples suggest that the HIMU source is preferentially enriched in Cl.

Because Nb should be largely retained in subducted oceanic crust during slab dehydration, we can use the average Cl/Nb ratio observed in inclusions from HIMU lavas (~18) to estimate a Cl concentration in recycled oceanic crust. For an average N-MORB Nb content of 5.6 ppm, we estimate ~100 ppm Cl in subducted oceanic crust after slab dehydration, intermediate between previous estimates of [1] and [3]. Given an estimated Cl content in altered oceanic crust of ~157-322 ppm [2], we estimate ~30-65% of the Cl in altered crust is retained in the slab after subduction-induced dehydration and eventually returned to the deep mantle.

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