Zircon as a magma mixing proxy: Textural, chemical and isotopic evidence from a young plutonic system

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Ion microprobe U-Pb zircon analyses of the Miocene Monte Capanne Plutonic System (MCPS, Tuscan Magmatic Province, Italy) reveal a range of ages (ca. 7-10 Ma) pointing out to a protracted magmatic history (2-3 Ma; Daly *et al.*, 2007) where magma mixing is believed to have played a significant role. As a companion study, we have investigated the textural, chemical and Hf isotopic response of zircon to various magmatic processes, with particular emphasis on magma mixing. For this purpose, we are using CL, BSE imaging as well as electron microprobe chemical data on a variety of magma products, including mafic microgranular enclaves, host monzogranites, mafic (Orano) dykes and granite porphyries. Importantly, zircon ages for these components partially overlap, suggesting that zircon was transferred and/or recycled throughout the lifetime of the whole plutonic system. A variety of textures have been encountered (inclusion-rich cores, patchy-zoning, small and large scale oscillatory zoning, pristine cores) as well as an extremely large range of trace to minor elements compositions (e.g., Hf: 7159-21284 ppm, Y: 39-8661 ppm, U: 67-65319 ppm and Th: 0-46225 ppm). While partitioning of Hf is largely temperature-dependent, intra-grain variations (zoning) in other elements (P, Th, U, Y and HREE) are interpreted to reflect changes in melt chemistry due to mixing between mafic and felsic magmas, where growth/resorption of zircon was also associated with reactions between other accessory minerals (particularly apatite and monazite; Dini *et al.*, 2004). The chemical signature of the dominant oscillatory zoning texture suggests growth from melts relatively depleted in trace elements, emphasising the important role of crystal fractionation in the evolution of the MCPS. These interpretations are in perfect agreement with models involving other phases, namely plagioclase (Gagnevin *et al.*, 2004) and K-feldspar (Gagnevin *et al.*, 2005a, b).

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Sr/Ca as a proxy for temperature in the deep-sea coral *Desmophyllum dianthus*

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We test Sr/Ca as a proxy for temperature in the cosmopolitan deep-sea coral species *Desmophyllum dianthus*. Several individuals of recent coral from regions of the deep-ocean typified by near constant temperate were selected from existing collections. Sub-samples were removed from the most recent portions of each skeleton and subjected to a full trace-metal cleaning protocol. Skeletal Sr/Ca was determined using isotope-dilution on a Neptune (ThermoFinnigan) multi-collector magnetic-sector ICP-MS. Intra-run reproducibility of a deep-sea coral consistency standard was better than 1 ‰ (2s), an improvement over most existing ICP-MS and optical spectroscopic methods. Across 8 individuals of *D. dianthus* spanning a 12°C range of growth temperatures, skeletal Sr/Ca decreases linearly as a function of temperature (R^2 = 0.82) with a shallower slope than most surface coral calibrations. Applied to the new archive of deep-sea coral, the Sr/Ca temperature proxy has the potential to generate high-resolution records of past deep-sea temperature.

Oxygen gas-phase formation in iron chemical gardens

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In this work we have employed the chemical gardens reaction as a laboratory device for *in situ*, follow the mixing of aqueous solutions of iron salts with sodium silicate and to characterize the reaction products by SEM HREM, XRD and XPS.

Chemical gardens are well known tubular structures formed in reaction–precipitation systems given rise to the formation of colorful, plant-like aggregates. Moreover, recent investigations have contributed to a renewed scientific interest in these self-organised structures. Although the reaction in chemical gardens is largely driven by pH gradients between the dissolving iron salt and the Na-silicate, recent works suggest that a strong redox processes can also take place during the formation of iron-silicate membranes.

One intriguing aspect related with silica gardens formation is the presence of small bubbles that are, in some instances, attached to the surface of the silica membranes, thus acting as templates for the formation of hollow tubular structures.

The aim of this research was to experimentally verify the composition and mechanisms of bubbles formation on Fe-Silica garden. From experiments performed in strictly anoxic conditions we will show that O_2 gas bubbles are still formed inside the microtubular structures as result of redox surface reactions taking place during the formation of colloidal membranes. In situ determination of iron species by UV-VIS showed the presence of Iron(VI)-ferrate oxyanion. Thus, a model for O2-bubble formation in silica garden is proposed, based on the rapid reduction of Fe(VI) to Fe(III) species through the of the strong pH gradient taken place across the silica membrane. Implications of these results for the formation of Fe-silicate phases in anoxic sedimentary environments will also be discussed.
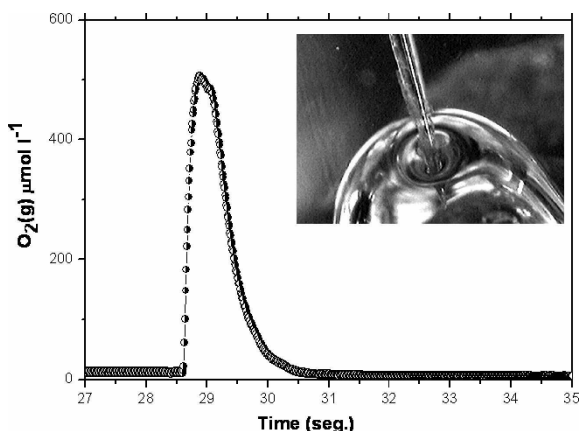
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The double-spike cookbook

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In recent years there has arisen considerable interest in exploring natural stable isotope fractionation of "non-traditional" elements. Here, the techniques of standard/sample bracketing or addition of a second element in the mass range (e.g. Cu with Zn) can be used on MC-ICP-MS instruments, but not TIMS. But the obvious method of choice in terms of accuracy – as well as simplicity in preseparation chemistry – is to add a double spike (DS) of the same element to the sample. The DS "freezes in" the natural fractionation at the time of its addition, and is thereafter insensitive to any chemical or instrumental fractionation.

The natural fractionation is solved for via mass balance of 3 independent isotope ratios (effectively a 3D isotope space). The DS technique can thus be used for any element with four or more isotopes—or 33 elements in all. Nevertheless, it has been seriously underutilized, in part due to the unease of data reduction, but mostly from uncertainty in the choice of the double spike itself. The task is made all the more difficult from the sheer number of candidate double spikes and isotope spaces to consider. For example, for Fe there are only 4 such spaces, while for Sn, with its 10 isotopes, there are 840 possible isotope spaces. The rigorous "optimization" of any double spike problem, then, presents a formidable challenge.

What is presently hampering the widespread use of double spikes is a lack of a comprehensive solution to the problem. Here, I remedy the situation by tackling all 3868 isotope spaces of the 33 elements (201 isotopes) that can be double spiked. The approach yields (1) an estimate of the "best" mixture (M) to use within a given 3D isotope space (and its corresponding spike, S), along with (2) a "figure of merit" enabling comparison between different isotope spaces of each element. Together, these provide first-order answers to questions of what DS to use, what the optimal mixture is, and what isotope space yields the best error propagation? Exclusion of particular isotopes (e.g. isobaric interferences) becomes an easy task since all isotope spaces have been evaluated. The methodology contrasts with that of previous studies in two ways: first, the "optimal" mixture is explicitly solved for rather than the spike composition, and second, more rigorous criteria are used. Normal compositions (N) were taken from IUPAC. The "optimization" was performed by multi-dimensional numerical minimization using a penalty function approach. Four criteria are built into the function: (1) M should lie far from S and close to N, (2) the angle between the fractionation vector through N and the mixing line should be large, (3) the so-called "intersection angle" should be large, and (4) the absolute magnitudes of the 3 isotope ratios of M should lie close to unity. Once a promising DS has been identified, its performance as a function of spike-to-sample ratio can then be examined.

These calculations should remove a major obstacle to implementing the double-spike technique, and hopefully make its use more routine and *in vogue* in future stable isotope studies.

Geochemical and Sr-Nd-Hf isotopic variations in Tajikistan loess: In search of source and climatic proxies

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Late Tertiary to Quaternary loess-paleosol sequences provide invaluable record of the changing environment in continental areas during that time interval. Climatic proxies in loess-paleosol sequences have been retrieved by a number of ways, including pollens, grain-size analysis, clay minerals, carbonate or organic matter contents or magnetic susceptibility. Loess source proxies include quartz morphology, heavy minerals assemblages, major and trace elements and Sr-Nd isotopic compositions. Some proxies are useful both as dust source proxy and as climatic proxy. We have been studying various loess-paleosol sequences in the Chinese Loess Plateau (Gallet *et al*. 1996, Jahn *et al*. 2001). On these sections we tested and proved the usefulness of geochemical and isotopic tools in loess research. Recently we extended our area of investigation to Central Asia, and the Chashmanigar (Tajikistan) loess section was chosen because some detailed stratigraphic and magnetic susceptibility data have been published by Ding *et al.* (2002). This section is about 200 m thick and consists of an alternation of loess and paleosol layers. A combination of geochemical and isotopic data is used to trace back the source(s) of these eolian deposits and their weathering history. Isotopic data (Sr-Nd-Hf) for whole-rock samples and for chemically separated fractions allow to document the change in protolith composition in response to climatic and tectonic events in the area. Major-elements, organic matter and carbonate content were measured on whole-rocks samples. Preliminary results show that our previous understanding of loess-paleosol geochemistry, first established on the Loess Plateau of China, is still valid here. Pedogenesis is clearly distinguished by the depletion or relative enrichment of a number of chemically mobile elements. There is a direct relationship between magnetic susceptibility increase in paleosol and depletion/enrichment of some chemical elements. We are currently working to translate this relationship into more quantitative laws.

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The effect of variable source of terrestrial organic carbon on geochemical records of atmospheric level of CO_2

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Carbon isotope analyses of fossil plants ($\delta^{13}C_{plant}$) have been widely used as chemostratigraphic and palaeoenvironmental tools. It has even been suggested that $\delta^{13}C_{plant}$ can be used as a proxy of $\delta^{13}C$ of palaeo-atmospheric CO_2 [1-2]. This parameter is an important variable for calculating p_{CO2} from the $\delta^{13}C$ of soil carbonate [3], the current largest database on records of atmospheric level of CO_2. However, the $\delta^{13}C$ of modern plants varies between species and palaeo-studies have attempted to go around this issue by focussing on monospecific dataset through time [4].

Here, we present evidences that in addition to species, the provenance of the woody debris will also introduce a significant variability in $\delta^{13}C_{plant}$. The transfer of particulate organic carbon (POC) has been studied in suspended material carried by small rivers draining active mountain belts (Southern Alps, New Zealand and Taiwan). In this active mountain belt, sediment discharge is dominated by landslide-derived material. The altitudinal spread of these landslides means that the POC samples vegetation dominated by C3-type plants and therefore having a variable $\delta^{13}C_{plant}$ [5]. Our sampling of pine trees along and altitudinal transect in Taiwan shows a range of in $\delta^{13}C_{plant}$ of 2‰, in line with previous findings [5]. The $\delta^{13}C$ of the POC in a single river sampled throughout the rainy season in Taiwan ranges from -21.5 to -25‰, while the range is >5‰ in Western Southern Alps. Of course not all of these variations can be attributed to a variable isotopic composition of the vegetation and the fossil component can be as large as 90%. But in some Taiwanese rivers this fossil component corresponds to the recycling of Miocene woody debris. Based on these observations, we would argue that the use of $\delta^{13}C_{plant}$ for calculating p_{CO2} is of very little help and also that it can be misleading in chemostratigraphy.

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Diel iron cycling in acidic rivers of southwestern Spain

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Background

In June 2006, diel sampling was conducted on the Tinto, Odiel, and Agrio Rivers of Huelva Province, Spain. These rivers are highly acidic due to acid rock drainage from massive sulfide deposits of the Iberian Pyrite Belt (Cánovas *et al*., 2007). Variables quantified included streamflow, temperature, pH, Eh, photo-synthetically active radiation, and concentrations of dissolved and total metals, anions, Fe(II)/Fe(III), and As(III)/As(V).

Results

Average 24-h pH values were 2.36, 2.30, and 3.04 at the Tinto, Agrio, and Odiel Rivers, respectively. Both pH and streamflow were essentially constant with time in each river. The only solute that showed a robust diel concentration cycle in all three rivers was dissolved Fe(II). Concentrations of Fe(II) at mid-day were 1.8 to 28 times higher than concentrations in the early morning (pre-dawn). The daytime $m_{Fe(II)}$ increases were most likely caused by photoreduction of dissolved or solid-phase Fe(III). The night-time $m_{Fe(II)}$ decreases were attributed to biologically catalyzed re-oxidation of Fe(II) to Fe(III). First-order rate constants of $(2 \text{ to } 7) \times 10^{-5} \text{ sec}^{-1}$ for the bacterial oxidation of Fe(II) were estimated from the observed decreases in $m_{Fe(II)}$ during the night. Maximum rates of bacterial Fe(II) oxidation (estimated to be > 3 μmol/L/h) occurred at mid-day. This amount of Fe(II) oxidation can support a growth rate of over 10^6 cells/L/h for *At. ferrooxidans*, the dominant procaryote in the Tinto River (López-Archilla *et al*., 2001).

Conclusions

Photoreduction plays a key role in biogeochemical cycling of Fe in the Tinto and neighboring rivers, and it has not been reported in previous geochemical and ecological studies of this extremely acidic and Fe-rich environment (e.g., Amils *et al*., 2007). Further work is needed to quantify the relative rates of Fe(II) production by photoreduction and by heterotrophic Fe(III)-reducing bacteria. The results of this study have implications for the primitive life that may have existed in acidic aqueous environments on early Earth or other planetary bodies such as Mars.

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Interaction of the magma with the sedimentary wall rock and magnetite ore genesis in the Panzhihua mafic layered intrusion, SW China

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The Panzhihua intrusion is a gabbroic Fe-Ti-V oxide ore-bearing sill associated with the Emeishan flood basalts in SW China (Zhou *et al*. 2005). It is overlain by a syenitic body and it concordantly intrudes late-Proterozoic dolomitic limestones, remnants of which can be found as metamorphosed xenoliths in the gabbroic body. Compositions of metasediments from the contact aureole show evidence for a pronounced transfer of certain major and trace elements between magma and sediments, perhaps linked to hydrothermal circulation driven by magma emplacement.

Numerical modeling with PELE (Boudreau, 1999) shows that when magma with the average chemical composition of Emeishan basalt fractionally crystallizes under oxidising conditions (oxygen buffer > FMQ) and/or with high water contents, magnetite appears early in the crystallization sequence. This is a condition for an efficient segregation of magnetite and for the formation of the ore deposit.

Mineralogical and chemical studies of the contact aureole demonstrate that footwall dolomites were degassed during intrusion of the gabbro. We propose that CO_2-rich fluids released by this degassing increased the oxygen fugacity of the magma and caused early and massive crystallization of magnetite.

Because magnetite crystallized when the intrusion was largely molten, it migrated to the base of the gabbroic body. The increase of the viscosity in the magma and the decrease of its density during the late stages of crystallization promoted the segregation of evolved felsic liquids that solidified as syenite intrusions. The association of gabbroic and syenitic bodies in Panzhihua region results from fractional crystallization of common parental magmas.

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Stability of hydrous ringwoodite in the Martian mantle

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Introduction

Branching networks of valleys and huge outflow channels on Mars provide evidence for the previous existence of water on its planetary surface. The water was probably once stored in the Martian interior and was then liberated to the surface. To understand this process, knowledge of Martian mantle structure and stability of hydrous phases is required.

Experiments

In order to identify possible hydrous high-pressure minerals in the Martian mantle and to determine their stability fields, we have conducted a series of multi-anvil experiments at the Bayerisches Geoinstitut, University of Bayreuth. First experiments were performed at pressures of 15 to 18 GPa and at variable temperatures between 750°C and 1150°C using a mixture of $2 Mg(OH)_2 + Fe_2SiO_4 + SiO_2$ as starting material. Experimental run products were examined by transmission electron microscopy, microprobe, IR and RAMAN spectroscopy.

Results and discussion

At 15 GPa and temperatures between 750° and 1150 °C cubic ringwoodite exists as single phase. Microprobe analyses yield the expected ringwoodite composition nominally equivalent to Fa48. At 18 GPa and 950 °C we observe a change to the three-phase assemblage ringwoodite + wüstite + stishovite, while the specimen compressed to the same pressure was melted at 1150°C. In comparison to the dry, Mg-rich system [1], the enhanced iron and water contents lower thus the transformation pressure by 3 GPa (from 21 GPa to 18 GPa) as well as the liquidus temperatures by at least 500°C. IR spectroscopy attests to an uptake of about 2800 ppm H_2O. To understand the incorporation mechanism of water we have also used Fe L_{32} electron energy loss spectroscopy, revealing that the iron is purely ferrous. Thus, the water is probably accommodated by the replacement of Mg^{2+} by $2H^+$.

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Application of the field seismic data in the security assessment of coal mining in Marbi Area

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Introduction

The Marbi area is located in Shanxi Province in north China, where plenty of coal resources are mined. In the past dacades, a large amount of seismic exploration work with the aim at coal recources has been done in the area successively. Based on the foundation of seismic exploration data, this study focuses on the structure of sedimentary basin and the security assessment of coal mining in the Marbi area.

Experiment and Results

Our data processing, combined with the existed local geological information, can be summarized concisely into the following steps (Claerbout, 1985; Ecker *et al.*, 1996; Li *et al.*, 2006): (1) carefully checked the positions of field shot-receiver pairs to obtain accurate localities; (2) calculated the static corrections in details; (3) eliminated bad shots, bad courses and abnormal amplitudes; (4) selected appropriate deconvolution parameters; (5) made accurate velocity analysis and got residual static corrections through stacking; (6) carried out the post stack processing and precise migration.

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

Acknowledgment

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Recycling deep cratonic lithosphere and generation of intraplate magmatism

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Recycling continental lithosphere via foundering is suggested to be an important geodynamic process but is difficult to document (Sobolev *et al*., 2005). Here we show that Early Cretaceous alkaline picrites and high-magnesium basalts from the North China craton provide evidence for such recycling. These mantle-derived lavas contain both xenocrystic and magmatic olivines. The former have high Fo_{92-93} and low CaO (<0.10%) and suggest derivation from the Archean mantle lithosphere. More importtnatly, these lavas contain unusual reversely zoned clinopyroxenes. Compositions of their low Mg cores and high Mg mantles are consistent with crystallization from eclogite- and peridotite-derived melts, respectively. The cores are high in Na_2O (up to 2.4%) and frequently contain ilmenite exsolution lamellae, whereas the mantles are low in Na_2O (<0.92%) and lamellae-free. These lines of evidence suggest that the cores formed at a significantly greater depth (≥ 2.5 GPa) than the surrounding mantles (≥ 1.5 GPa). The whole-rock compositions of the basalts also contain chemical evidence (high Ni/Cr, Fe/Mn, Sr/Y La_N/Yb_N, and Th/U ratios and low Lu/Hf ratio) for their derivation from an olivine-free source and incorporation of melts derived from foundered eclogitic lower continental crust. Together with our previous studies of the late Jurassic high-Mg intermediate to felsic lavas from western Liaoning in the northeastern North China craton (Gao *et al*., 2004), these findings indicate that thinning of the North China craton was caused by recycling of the lower lithosphere (mantle and lower crust), and demonstrate that continental lithosphere recycling is a viable means of producing mantle heterogeneity.

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The building-up exercise of a thermodynamic data set on ISA-actinide system

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Isosaccharinic acid (ISA) is one of the most important degradation products of cellulose expected in the hyperalkaline conditions defined by cementitious environments. Despite the high affinity shown by this ligand toward actinides complexation, the number and reliability of available experimental studies is still limited (Hummel *et al*., 2005). Due to the potential effect of these complexes in the performance assessment exercises, this work aims at providing a comprehensive and coherent thermodynamic data set on the ISA-actinide system. For this purpose, the thermodynamic data available in the literature have been complemented with further modelling exercises and estimations based on ionic radii correlations among actinides.

Under slightly reducing conditions and absence of carbonate and calcium, $M(OH)_xISA_y$ ternary complexes (M= Th, U(IV), Np(IV), Pu(IV)) are expected to dominate aqueous speciation. The available publications show a moderate agreement among the stability constants of these complexes, although their structure is still ill-defined and some authors propose complexation reactions where the alcohol groups of ISA are partly deprotonated. Under hyperalkaline conditions and the presence of calcium, the species $CaM(OH)_4ISA_2(aq)$ has been described for Th and may dominate aqueous speciation of further tetravalent actinides.

The limited number of experimental studies assessing the complexation of An(V) and An(VI) with ISA indicates the possible formation of $An(V)O_2(OH)_x(ISA)_y-$ and $An(VI)O_2(OH)_x(ISA)_y$-like complexes.

This work has allowed to obtain a complete set of stability constants for complexes of ISA with tetravalent actinides under alkaline to hyperalkaline conditions. Similarly, stoichiometries and stability constants for An(V)-ISA and An(VI)-ISA complexes have been proposed, although further experimental efforts would be advisable to gain confidence on these complexes.

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Experimental determination of C_l/C_o of Rb, Sr and Ba and comparison with C_l/C_o of a migmatite

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Introduction

As a way to settle the difficulties regarding the origin and evolution of granitic rocks, we studied the C_l/C_o values of Rb, Sr and Ba from melts of the Ollo de Sapo Gneiss (modal comp.: Qtz: 42; Pl (An$_{19}$): 20; Kfs: 8; Bt (Mg$_{40}$): 10; Ms: 20) at 6 and 10 kbar, 750, 800, 850 and 900 ºC, and 10% wt water. Experiments were run in a piston-cylinder apparatus at the High Pressure Laboratory of the University of Huelva, and analysis were made using an ICP-MS of the Central Services of the University of Huelva.

A diamond trap has been used to separate melt from residual minerals, so a pressure gradient between powder and trap (which can be a source of disequilibrium) exists, but disappears or is minimised if melt soaks the trap and residual minerals. Thus, melting process begins as a fractional melting followed by a batch melting if melt quantity exceeds a critical amount.

Discussion

At 6 kbar, C_l/C_o values for Rb are lower than 1 (0,67-0,98) with a minimum at 800 ºC due to the high productivity of melt by the breakdown of feldspars; for Sr, C_l/C_o is upper than 1 (1,01-1,43) and tends to this value with increasing melting amount; for Ba, C_l/C_o is upper than 1 (1,01-1,24), with a maximum at 800 ºC. Comparing these values with calculated for High Himalayan leucogranites, assuming a greywacke source in presence of water, a clear resemblance for Rb and a difference for Sr and Ba can be seen.

Conclusion

The election of the K_D values has a decisive influence in C_l/C_o values, although this discrepancy can also be due to a disequilibrium melting because of the diamond trap.

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Radium isotopes as tracers of submarine groundwater and nitrogen discharge in a karstic area

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Introduction

A mass balance for ^{223}Ra ($T_{1/2}$=11.4 d) and ^{224}Ra ($T_{1/2}$=3.66 d) is applied to a karstic area (*Badum*, Spain) to evaluate the submarine groundwater discharge (SGD) through coastal springs. The strategy is based on the enrichment of Ra in groundwater compared to surficial waters.

Ra isotopes were measured from coastal, brackish springs and seawater samples by using a *Radium Delayed Coincidence Counter* (Moore and Arnold, 1996).

Results and discussion

All coastal samples are enriched in radium activities compared to the open sea, the highest activities being found in the springs. ^{223}Ra and ^{224}Ra concentrations are highly correlated and Ra vs. salinity plots suggest a mixing process between the springs and the coastal sea endmembers (Fig. 1). A Ra mass balance allows obtaining a groundwater fraction of 38%. By considering this fraction, the water residence time (0.5 d) also derived from the short-lived Ra isotopes and the sampled water column, a SGD flux is calculated to be $5 \cdot 10^6$ m^3 yr^{-1}. This flow accounts for a nitrate input of 3 mmol m^{-2} d^{-1}, which is comparable with literature values of SGD-derived nitrogen inputs to coastal areas (Charette and Buesseler, 2004).

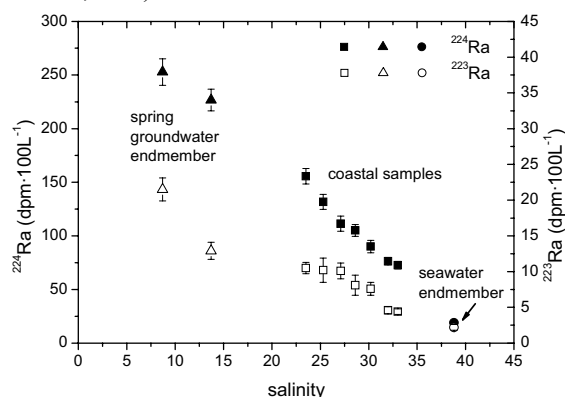**Figure 1.** ^{223}Ra and ^{224}Ra activities in all water samples indicate the two endmembers.

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Charette M.A. and Buesseler K.O. (2004), *Limnol. and Oceanogr.* **49(2)** 376-385

Short-term geochemical variation within a single eruption event: Mount Edgecumbe volcano, Bay of Plenty, New Zealand

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A re-evaluation of the petrogenetic links between the andesites and rhyolites from the Taupo Volcanic Zone of New Zealand's North Island by Price *et al.* (2005) led to the proposal of an evolutionary pattern from andesite-dominated to rhyolite-dominated magmatic systems with time.

In order to understand the processes involved in this long-term shift towards catastrophic rhyolite eruptions, we must first ensure that we fully comprehend the factors controlling short-term variations. However, detailed, stratigraphically controlled sampling of well-documented single eruptive episodes and eruptive sequences has revealed considerable internal complexities at several arc-type volcanoes.

Here we present analyses of multiple samples from an accurately dated, (3115±35 yrs BP, Carroll *et al*. 1997) andesitic block- and ash-flow deposit on Mount Edgecumbe at the active volcanic front of the TVZ. Our results are based on whole-rock analyses for major element oxides, trace and rare earth elements in addition to Sr and Nd isotope ratios resolving the extent of geochemical variability within a strict time-frame.

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Cooling rates contraints on the accretion of the plutonic crust at fast-spreading mid-ocean ridges

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We report the results of a thermo-mechanical model of crustal flow beneath fast spreading mid-ocean ridges considering the effect of deep, near off-axis hydrothermal cooling and variable igneous accretion modes. The accretion mode determines the flow lines along which gabbro crystallize and the lateral advection of heat and mass. Near, off-axis hydrothermal cooling determines the shape of the magma chamber and viscosity, which influence the stream function and the shape of flow lines along with plutonic gabbro crystallize. The cooling rate of the plutonic crust along a flow line depends on the velocity and geothermal gradient along it, which are in turn imposed by: (i) the accretion mode, (ii) the extend of off-axis hydrothermal cooling, and (iii) conductive thermal rebound far from the ridge axis. The conventional wisdom that the igneous and metamorphic cooling rates of exposed sections of lower oceanic crust are similar and both reflect the on-axis thermal cooling of the oceanic crust is too simplistic. The cooling history is inherently related to the method used to retrieve it; particularly to the temperature interval recorded by the method. The cooling history may integrate cooling at different depths at distances from the ridge axis, which are not necessarily those of their final depth of emplacement. While igneous cooling rates record the thermal structure of the magma chambers, metamorphic cooling rates may record different extend of the off-axis thermal structure depending on the effective temperature of diffusion initiation and closure temperature. Igneous and metamorphic cooling rate variations with depth are markedly diferentent for a given accretion mode and, if available, both might be used to discrimante among different scenarios proposed for the accretion of the oceanic crust a fast-spreading mid-ocean ridges.

Thermodynamic modelling the sorption of heavy metals and actinides onto clay minerals by Gibbs energy minimization approach

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One of the major aims in the development of sorption models was to set up the simplest chemically reasonable model with the least number of variable parameters capable of describing and predicting sorption over a wide range of conditions. In this study we have investigated the sorption of heavy metals and actinides onto montmorillonite, illite and kaolinite in aqueous solutions by applying the Gibbs energy minimization computer code "HCh" (Yu.V. Shvarov, Moscow State University) via a non-electrostatic model. The emphasis is made on the named clay minerals because of their importance in terrestrial weathering processes and designed industrial applications. The thermodynamic model combines cation exchange at a permanent negatively charged sites and pH-dependent surface complexation at the amphoteric edge-type sites. Site types, their individual capacitance and the acidity constants associated with them, were considered to be non-adjustable parameters and were fixed in all of the calculations: the cation exchange capacity (CEC) is 0.9, 0.25 nd 0.05 equiv/kg and equal to concentration of exchangeable sites NaX; the aluminol (>AlOH) and silanol (>SiOH) edge-type sites are responsible for the surface complexation, and their total density is a part of a CEC (0.09, 0.1 and 0.05 mol/kg). The equilibrium constants for the adsorption and ion exchange reactions could be found due to correlations with the aqueous hydrolysis constants.

The calculated sorption models showed good approximation of experimental distribution coefficients of majority sorbates onto named three clay minerals. We note that the model parameters discussed here are closely dependent on the decisive variables, namely the surface site capacities. Indeed, the value of the CEC and the density of edge sites directly control the metal uptake by considered clay minerals. It allows to show that: a) the influence of ionic strength and pH of solutions on the metal sorption is differentiated depending on the crystallochemical type of clay mineral. The more sorption capacity of a phase, the influence of concentration of electrolyte is more strongly revealed. As a result, kaolinite could be successfully used in the solutions with I > 0.1 and pH > 5 instead of montmorillonite, which exhibits the highest exchange capacity; b) the sorption show a higher difference in selectivity of the cations in the pH range 4-8, where it is greatly affected by the element chemical properties (affinity to the hydrolysis in solutions and the surface-binding complexation); c) on the contrary, at weakly acidic pH of diluted solutions (low ionic strength), selectivity coefficients Kc could be accepted the same for analogous type of cations, if was not determined exactly. Usually, Kc values for bivalent-monovalent exchange are ~3 to 4 and for bivalent-bivalent exchange around unity.

The Bicaz lake (Romania): Hydrodynamics and trace element behaviour

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The dammed lake of Bicaz (East Carpathians, Romania), presents the following physical characteristics: 31.1 km length, 2 km wide, water volume of $1.150 \cdot 10^9$ m^3. The Bistrița river is the main tributary with a mean water contribution of $1.721 \cdot 10^9$ m^3/year and a mean suspended matter flow of 291,000 tons/year. This river drains a catchment rich in formerly mined mineralizations of polymetallic sulfides.

Three locations, an upper, a middle, and a down site as well as the main tributary river were sampled for one hydrological year.
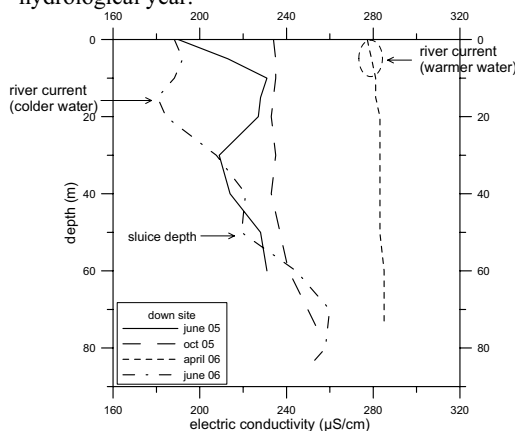
The electric conductivity and the concentration of major ions allow to evidence a water layer whose position varies along the lake and according to season (water temperature and lake depth). This current which originates from the Bistrița river is intensified by the sluice drawing off. The distribution of Fe between dissolved and particulate forms, along the lake and for each season, and the distribution of Mn, excepted in some cases, show the lake is mainly oxidizing. In the dissolved phase, the concentration of Fe and Mn is smaller than in the river. Some trace elements such as Cr and V occur mainly in the particulate form, and are enriched in the dissolved phase compared to the Bistrita. On the contrary, Ni, As and U are found mainly in the dissolved phase: Ni is enriched compared to the river whereas As and U are similar. The distribution of Co between particulate matter and solution is variable and does not follow Mn. The concentration of Co in the dissolved phase is smaller than in the river.

Thus, stratification of the water column within the lake is disturbed by the river current and by the sluice. The weak relationship between Fe and Mn and analyzed trace elements may be linked to hydrodynamics of the lake.

A radium and radon investigation of the submarine estuary under Venice

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Submarine groundwater discharge (SGD) is now recognised as a major pathway for nutrients and contaminants. Mass balance models based on excesses of natural radioactive isotopes in coastal environments (estuary, lagoon) can provide integrated estimates of SGD. In this work, we measured ^{226}Ra and ^{222}Rn activities in the southern part of the Venice lagoon, a most emblematic case of highly vulnerable coastal flatland heavily impacted by anthropogenic activities.

^{226}Ra activities measurements were performed by isotope dilution and thermal ionization mass spectrometry on small samples (0.5L). Very small variations in ^{226}Ra can be resolved by this technique, thanks to the high precision that is attainable (1 to 5% on 20 to 200 fg samples). ^{222}Rn activities were measured by in-situ continuous-monitoring α-counting technique with a precision of 10%.

^{226}Ra and ^{222}Rn activities are significantly higher in the lagoon samples (2.3-5.3 and 26-82 Bq/m^3 respectively) than in the open Adriatic Sea (2.2 and 10 Bq/m^3 respectively). Mass balance models taking into account riverine inputs, diffusion from sediments, loss, production and decay of the isotopes, do not explain the lagoon excesses and suggest the existence of another source of ^{226}Ra and ^{222}Rn in the lagoon.

Groundwater from the semi-confined aquifer (0-30 m) connected with lagoon waters presents significant enrichment in ^{226}Ra and ^{222}Rn (c.a. 35 Bq/m^3 and 1300 Bq/m^3), and may be considered as an additional source to generate the required excess. Using these activities, the input of groundwater necessary to explain the observed excess in the lagoon is 5.2×10^5 and 5.5×10^5 m^3.d^{-1}, based on ^{226}Ra and ^{222}Rn mass balance respectively. Furthermore, Rn monitoring during tidal cycles shows that the excess activity is produced during the falling tide, when aquifers significant discharge interstitial waters through the sediments.

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Cryptic zoning in garnets from the Nufenen Pass area

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Garnets from graphite rich black shales of the Mesozoic cover of the Gotthard Massif in the Swiss Alps display textural sector zoning with birefringent lamellae emanating from sector boundaries. Central sections of garnets cut along [110] display 6 sectors, which are in places crowned by a graphite rich cap. The birefringent lamellae are oriented normal to the sector end face. Individual lamellae have a length of up to 300 microns and a thickness of typically 10 microns. The lamellae have an elliptical cross section of a few tens of microns for their long axis on sections parallel to the sector end face. A cross hatched pattern is created with lamellae orientations parrallel to the edges of the sector walls. Lamellae are absent in the graphite inclusion rich rim. EPMA analysis of the birefringent lamellae show that they are Ca richer than the adjacent isotropic lamellae which are Fe richer. The composition difference in calcium and iron between the two type of lamellae can be up to 0.2 cation per formulla unit. The lamellae are zoned along their length, following the overall garnet zoning pattern. Composition ranges for the two lamellae overlap for a single garnet.

The coexistance of two garnet composition and structure could be explained by a miscibility gap in the solid solution or by crystallisation of one or two metastable precursors. The composition difference between the two type of lamellae is too small to reflect a miscibility gap and lamellae composition overlap. Hence they are not exsolutions. Other type of zoning have been explained by the replacement of heterogeneities in the matrix or concentric zoning due to rythmically changing conditions (Yardley *et al.*, 1996). The crystallographic orientation of the lamellae indicates that they do not represent replacement of matrix heterogeneities. The orientation of the lamellae demonstrates, that at any time, both types of lamellae were crystallizing.

We propose an alternate mechanism for this case. Two garnets with a slightly different composition and structure nucleate topotactically on the surface of a growing garnet with a similar probability. It is enough that continued nucleation of a new garnet layer slightly prefers the same structure to assure a fiber-like growth of both compositions side by side.

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Water solubility in clinopyroxene

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Clinopyroxenes, in particular omphacites, have the highest water contents among the minerals from mantle xenoliths. In subducting slabs, water in omphacite may contribute significantly to the recycling of water into the mantle. We have therefore measured the solubility of water in both pure $CaMgSi_2O_6$ diopside and in diopside containing variable amounts of aluminum as Ca-Tschermak $CaAlAlSiO_6$ component. Single crystals of the pyroxenes were grown in piston-cylinder and multi-anvil experiments using oxide/hydroxide mixtures with excess water as starting materials. Water contents were quantified from polarized infrared spectra of clear single crystals.

Water solubility in pure diopside is rather low, in the order of a few hundred ppm at 1.5 – 3 GPa and 800 – 1100 ˚C. The type of infrared spectra observed varies with the bulk composition of the sample. Diopside crystals synthesized with excess silica show several bands at low frequency between 3280 and 3480 cm⁻¹. These bands are attributed to protons on Ca or Mg vacancies. Diopside crystals synthesized with excess MgO or a deficiency of SiO_2, which coexist with olivine, show only one sharp band at 3650 cm⁻¹. This band is therefore probably due to protons associated with silica vacancies.

Water solubility in diopside strongly increases with alumina content and reaches up to 3000 ppm already at 1.5 GPa (Fig. 1). Aluminous diopside samples only show one infrared band at 3650 cm⁻¹, corresponding to the substitution of $Al^{3+} + H^+$ for Si^{4+}. Our data therefore confirm that Al in pyroxenes largely controls water storage in the uppermost mantle.
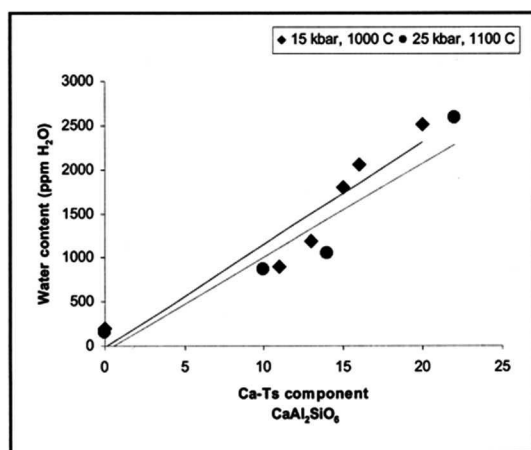

Figure 1. Water solubility in aluminous diopside as function of the content of Ca-Tschermak component (in mol %)

Cosmogenic ³He production rate in pyroxenes and olivines at low latitude

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In the past decade cosmogenic ³He has become a widely used chronometer of surface exposure. The low cost of noble gas measurements and the relatively high production rate in mafic minerals have, in particular, been exploited for dating exposure of basaltic rocks. Cosmogenic ³He production rate in olivine is well documented, however, only few studies have been dedicated to the determination of the production rate in pyroxene (i.e. [1-2], 39-46˚N and 47˚S latitude). The study presented here is designed to measure long-term cosmogenic ³He production rate in pyroxenes and co-existing olivines at low latitudes, and to document the variation of cosmogenic ³He production rate with chemical composition.

Four olivine- and proxene-rich basalt flows between 132 and 482 m altitude were sampled from Ascension Island (7.5˚S) where the arid climate preserves ropey-flow tops. In pyroxenes, cosmogenic ³He concentrations were calculated using (i) the magmatic ³He/⁴He released by in vacuo crushing and melting, and (ii) the ⁴He concentrations measured by melting. The magmatic ³He/⁴He is remarkably constant ($6.8\pm0.4\ R_a$) while the ³He/⁴He of melt extractions range from 100 to 500 R_a, suggesting that the correction for non-cosmogenic He is minimal. Cosmogenic ³He concentrations in multiple pyroxene samples from each flow range from 1.41 x 10⁷ to 2.69 x 10⁷ atoms/g, corresponding to approximately 220 to 350 kyr exposure. Error-weighted mean values have total uncertainties of 5% implying that the flow tops have not been significantly covered or eroded. Measurements of cosmogenic ³He concentrations in olivines from the same samples will be conducted and compared to the pyroxenes to constrain the cosmogenic ³He production rate in pyroxenes and to explore the production rate variation with chemical composition.

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Actinide geochemistry: From the molecular level to the real system

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Geochemical processes leading to either mobilization or retention of radionuclides in an aquifer are significantly influenced by their interaction with rock, sediment and colloid surfaces. Therefore, performance assessment of nuclear waste disposal requires the elucidation and quantification of those processes. State-of-the-art analytical techniques as e.g. laser - and X-ray spectroscopy are increasingly applied to study solid-liquid interface reactions and to obtain molecular level speciation insight.

We have studied the sorption of trivalent lanthanides and actinides (M(III)) onto aluminium oxides, hydroxides and purified clay minerals by the time-resolved laser fluorescence spectroscopy and X-Ray-Fluorescence spectroscopy [1, 2]. Chemical nature and structure of surface bound actinides are proposed based on spectroscopic information. Similarities of spectroscopic data obtained for M(III) sorbed onto γ-alumina, gibbsite and clay minerals suggest the formation of very comparable inner-sphere surface complexes like $\equiv$S-O-An(III)(OH)$_x^{(2-x)}$(H$_2$O)$_{5-x}$ at pH > 5. Those speciation data are found consistent with those predicted by surface complexation modelling. The applicability of data obtained for pure mineral phases to actinide sorption onto heterogeneously composed natural clay rock is investigated by experiments and by geochemical modelling.

The assessment of clay colloid borne actinide migration observed in the frame of in-situ experiments at the Grimsel underground laboratory [3] also calls for detailed information on actinide speciation. Combined spectroscopy and wet chemistry experiments provide a fairly consistent picture of the actinide speciation under given groundwater conditions and impart insight into the dynamics of actinide-colloid interaction. Notably for tetravalent actinides we observe significant impact of ageing on the rate of actinide desorption from clay colloids. Studies are ongoing to elucidate underlying mechanisms.

Above mentioned studies demonstrate the appropriateness of combining spectroscopy and wet chemistry as an appropriate strategy to validate geochemical model assumptions and to reduce uncertainties.

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Microbial reduction of arsenate with sulfide as electron donor at neutral pH

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Arsenic is a common trace element found in most natural waters, as well as a documented human carcinogen. In the environment, arsenic occurs in the valence states As(V) and As(III). The bioavailability of arsenic is in general controlled by the presence of iron, by sorption of arsenate (As(V)) to iron minerals, and sulfide, resulting in the precipitation of arsenite (As(III)) as arsenic sulfides.

It is well known that arsenate may be microbiologically reduced under anaerobic conditions, and recently microbial reduction of arsenate coupled to the use of sulfide as electron donor was described [1, 2]. This process occurred in soda lakes, with pH 10 and high salt concentration, conditions under which sulfide is less toxic due to the virtual absence of H$_2$S. Chemical reduction of arsenate with sulfide has been shown to take place at acidic to neutral pH.

We investigated the possibility of biological reduction of arsenate with sulfide as electron donor at neutral pH. Batch incubations were set-up using anaerobic sediment amended with arsenate and sulfide. Arsenate was removed from solution in 5-9 days. In control experiments with autoclaved sediment, part of the arsenate in solution was removed, which may indicate relatively slow sorption of arsenate on soil particles or chemical reduction of arsenate.

Incubations in which arsenate conversion occurred were transferred to fresh culture medium several times and yielded stable enrichment cultures. In these enrichment cultures two dominant bacterial species were present. Application of molecular biological techniques showed that the two species were related to the genus *Sulfurospirillum* and to sulfate reducing bacteria belonging to the delta-proteobacteria. We aim to isolate these two organisms in pure culture and study their physiology and ability to reduce arsenate with sulfide in more detail.

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Hg accumulation in reducing sediments of the Mediterranean Sea: Trace metal and Hg isotope evidence

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Mercury (Hg) has a complex biogeochemical cycle involving multiple oxidation states with gaseous, dissolved, and particle-associated species. We investigated the effects of different redox conditions on Hg partitioning in the marine environment. We analyzed Hg concentration and isotopic composition, as well as concentrations of a suite of trace metals that are widely used as indicators of productivity and redox conditions, in sediments from a mid-Pleistocene sapropel sequence in the Tyrrhenian Basin of the Mediterranean Sea. During episodes of sapropel formation, high productivity and reducing conditions produce organic-rich sediments, with characteristic trace metal patterns.

Concentrations of Hg and other metals covary with total organic carbon (TOC) content, with a Hg enrichment factor of 3.9 in high TOC sapropels versus low TOC non-sapropels. Enrichment factors determined for other elements are 1.3-2.1 for Cr, Cu and Zn; 3.0-4.9 for V, Co, Ni and U; 5.0-8.0 for Mo and Cd; and 13 for Re. Hg concentrations in these sediments are highly correlated with trace elements normally associated with organic matter delivery (Co, Ni, Cu, Zn and Cd) as well as with elements associated with enrichment in reducing sediments by mineral precipitation and adsorption occuring below the sediment-water interface (V, Cr, Mo, Re and U) (Tribovillard *et al.*, 2006). The strong correlation between Hg and both suites of trace metals suggests that particulate scavenging and/or in situ precipitation contributes to Hg accumulation in marine sediments. If we specifically look at the variation in metal concentrations in only those samples with low TOC content deposited under oxic conditions (non-sapropel layers), we find that Hg does not covary with V, Cr, Ni, Mo, Cd, Re or U, but does covary with Co, Cu, and Zn. These patterns may be related to variations in terrigenous sediment sources or preservation of these metals in sediments.

We also explored whether Hg isotope values could provide insight into changes in Hg deposition between sapropel and non-sapropel layers. Preliminary isotopic analyses show that sapropels have lower δ^{202}Hg values (Blum and Bergquist, 2007) than non-sapropel layers (-1.1‰ vs -0.7‰). This likely reflects either a change in Hg sources or isotopic fractionation during redox transformations.

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Mobilisation and speciation of depleted uranium in water and soils

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Depleted uranium (DU) from penetrating ammunition was exposed to several environmental conditions in order to determine the binding forms of uranium as well as in its dissolved and solid forms.

In a first series fresh disks of DU were treated with a calcium phosphate solution. The results from time-resolved laser-induced fluorescence spectroscopy clearly show that metaautunite $Ca(UO_2)_2(PO_4)_2$ x 2-6(H_2O) has formed during alteration [1].

In a second experiment the corrosion and leaching of used up DU was investigated for three years in a column with a soil core. The columns were irrigated with synthetic rainwater.

The luminescence spectrum of a yellow material, which was crystallized at the soil surface was assigned clearly to be the mineral sabugalite $AlH(UO_2)(PO_4)_4$ x 16(H_2O).

In contrast to the luminescence spectra of the solid material the spectra of the uranium species in the dissolved samples could only obtained at temperatures below 220 K. From the shape of the spectrum and the emission maxima of the luminescence of seepage water samples it could be clearly concluded that the solution species are mostly uranyl carbonate species $UO_2(CO_3)_3^{4-}$ [2].

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NWA 2999, an angrite with unusual bulk chemistry or a new type of achondrite?

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Introduction

NWA 2999 is classified as an angrite based on mineralogy and oxygen isotopes [1]. Chemical data indicate differences in bulk chemistry to other angrites, making this a unique meteorite.

Chemistry

Major elements were determined by XRF, trace elements on a different sample by INAA. For analytical procedures see [2,3]. Compared to average angrite, the Mg content is significantly higher, Si and the refractory elements Ca, Al and Ti as well as P are much lower. Unlike other angrites, NWA 2999 has abundant FeNi-metal, and corresponding levels of Ir, Au, Ni and Co.

Interpretation

Mixing calculations with average angrite composition were performed: Delivering the excess siderophiles is possible by contributing 8 % of the mass by an iron meteorite. But this is unlikely, because it cannot explain the high Mg and the low Ca, Al and Ti contents.

Adding more than 60 % of a primitive meteoritic component would have diluted the refractory elements to the measured values and led to the high Mg, Cr and siderophile element contents. The added component could have lost its P by metal-silicate equilibration before the metal was incorporated in NWA 2999. However the assumption of more than 60 % of external matter is difficult to reconcile with the angritic oxygen isotopic data and the low contents of volatiles.

An alternative view is to take both components from the same parent body. A differentiated lithology with elevated Ti, Ca, Al and REE, but with low Mg, Cr and almost no Ni and Ir is mixed with a core-mantle component, high in Mg, Cr, Fe, Ni, Au and Ir of the same parent body. Mixing could be the result of a large impact on the APB.

Another yet possibility is an origin from a different, until now unknown parent body, which is similar to angrites with respect to mineralogy and oxygen isotopes.

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Physicochemical Speciation of Iron in the Baltic Sea

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Size fractionated classes of Fe in surface water at two stations, one in central Baltic Sea (the Landsort Deep) and one in Bothnian Sea, were measured from spring until autumn to evaluate temporal variations in the physicochemical speciation. Membrane filtration, cross-flow ultrafiltration and DGT (diffusive gradients in thin films) were among the applied techniques. Average concentrations for total, <0.22 and <1kDa Fe were 32, 7.0 and 5.9nM respectively at the Landsort Deep. For the Bothnian Sea, these figures were 96, 21 and 6.2nM. DGT-labile concentrations of Fe were significantly lower than <1kDa at both stations. This probably indicates that a large portion of the DGT-labile Fe was organic bound, which would slow down the diffusion rate. The DGT-labile Fe concentration was on average 0.6 nM at Landsort Deep, and 1.0 nM in the Bothnian Sea. If assuming that all DGT-labile Fe was bound to fulvic acids the concentrations becomes about 5 times higher, but still lower than <1kDa. No clear trends were observed for the DGT measured concentrations. In both areas the concentration of Fe in all but the DGT-labile fraction decreased 60-80% towards end of the sampling period. Average ratios between total Fe and <0.22μm were about 4-5 at both stations, but in the Bothnian Sea also a clear difference between <0.22μm and <1kDa was observed, indicating a significant colloidal fraction. At the Landsort Deep, a peak of <1kDa Fe was evident in end of July, despite stable total concentrations during the summer. A small peak of <1kDa Fe was also observed in the Bothnian Sea, but not as clear as in Landsort. These peaks coincide with drops in biomass, indicating that this is a mineralization event. We hypothesize that the difference in concentration between DGT-labile and <1kDa is caused by organically bound species that are influenced by the presence of phytoplankton.

Imperfect accretion during the giant impact stage of terrestrial planet formation

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In the standard scenario of planet formation, terrestrial planets are formed in two stages: the formation of several tens of Mars-sized protoplanets through accretion of planetesimals, and collisions among these protoplanets (called ginat impacts). Although the nature of giant impacts determines the final masses, spin parameters, and orbital elements of the terrestrial planets, all the previous *N*-body simulation of terrestrial planet formation (e.g., Chembers 2001, Raymond *et al*. 2004, Kokubo *et al*. 2004) have been based on the assumption of the perfect accretion, that is, colliding two protoplanets always merge without mass loss. Agnor and Asphaug (2004) performed 48 SPH simulations for mutual collision of $1 \times$ Mars-mass protoplanets. They showed that the two protoplanets bounce and escape to infinity for collision with relatively faster impact velocity (e.g., $> 1.4 \times$ escape velocity for 30 deg of the impact angle), and they estimated that more than roughly half of giant impact events are not coalescence events.

In order to incorporate the effect of imperfect accretion into *N*-body simulations, we need to know the accretion condition for various types of giant impacts. Using the special-purpose computers for gravitational *N*-body problems (GRAPE), we performed more than 1000 runs of impact SPH simulations for various mass ratios (γ), impact angles (ξ), and impact velocities (v_{imp}). From the results of more than 1000 runs, we formulated the boundary of v_{imp} between coalition and rebound as parameters of γ and ξ. We also formulated the mass(es) and orbit(s) of post-impact planet(s).

We applied the above formulation to the impact events obtained by Kokubo *et al*. (2006), and found that 261 out of 635 giant impacts, that is 41%, are not coalescence events. We will also report the effects of imperfect accretion on the final states of the terrestrial planets such as the largest mass and rotation velocity.

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Isotopic evidence for Silicon within the Earth's core

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We present the first isotopic evidence for Si within the Earth's Core. It has long been proposed that the Earth's core must contain significant quantities of light elements, such as H, C, Si, S and K [1]. The high Mg/Si of the terrestrial mantle has been used to argue that Si in particular is an important component in the core [e.g 2]. Recent estimates indicate that it contains as much as 5-7wt% [e.g. 3], and the partitioning of Si into the metallic core should yield isotopic effects because of differences in bonding of Si between metals and silicates.

We analysed the Si isotope compositions for different bulk silicate reservoirs of the solar system as sampled by chondrites, basaltic achondrites thought to come from Vesta and Mars, and basaltic rocks from the Moon and the Earth's mantle. The mean values of these reservoirs obtained for this study are in excellent accord with previous estimates, however, the spread in the data is an order of magnitude lower. A significant difference is found between the bulk silicate Earth (BSE) and Moon on the one hand and meteorites on the other.

It appears unlikely that this observed Si isotope shift can be produced by volatilisation processes during the early accretion history of the Earth. Rather, the observed Si isotope shift was probably produced during Si partitioning into the Earth's core. We modelled the potential Si isotope fractionation during silicate-metal partitioning and can show that both the direction and magnitude of such fractionations are consistent with the observed isotopic differences between BSE/Moon and meteorites.

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Resolving the evolution of a subduction zone: Eastern Srednogorie, SE Europe

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Eastern Srednogorie zone is the easternmost part of the mineralized ABTS (Apuseni-Banat-Timok-Srednogorie) belt in SE Europe. This belt is a former Late Cretaceous island arc that was formed during the process of northward subduction of the Tethyan ocean beneath the European platform. Compared to the other parts of the belt, magmatic products exhibit the most variable composition. However, the zone is the least studied, and here we present new geochemical, isotope and geochronological data with the aim to understand the genesis of the magmatism. We try to isolate the most primitive initial magmas that fractionated and assimilated parts of the crust to produce the abundant Late Cretaceous magmatism, and to trace the across-and along-arc change in the age and composition of the magmatism.

Magmatic products in the Eastern Srednogorie show the entire spectrum of rocks typical for island-arc environments. Based on their chemical composition three main regions are subdivided from south to north; (1) tholeiitic to calc-alkaline, basic to acid intrusives in the southern; (2) predominantly potassic to ultrapotassic mafic-intemediate volcanis in the central and (3) calc-alkaline basic-intermediate volcanics in the northern part. Trace and REE distribution patterns argue for subduction related magmatism for all rock varieties.

TIMS and LA-ICPMS dating of single zircon grains shows that magmatic activity started at about 86 Ma with few intrusions but the climax of the magmatism was in the Campanian (81-78 Ma). Whole-rock Pb and Sr isotopes of most mafic magmas show the least radiogenic compositions ($^{87}Sr/^{86}Sr_i$ of 0.7040, $^{206}Pb/^{204}Pb_i$ 18.38, $^{207}Pb/^{204}Pb_i$ 15.57 and $^{208}Pb/^{204}Pb_i$ 38.27). These values are less radiogenic compared to Late Cretaceos magmatic rocks of the adjacent Central Srednogorie zone. In addition, the majority of the analysed rocks contain Cretaceous zircons with positive εHf at 80 Ma (from 0 to +12), suggesting a mantle-dominated origin. However, these rocks contain variable amounts of inherited zircons with negative, crustal-like εHf at 80 Ma This fact clearly show that the rocks suffer some contamination by crustal-derived lithologies. The amount of crustal contamination increases with time. Potential candidates for the contaminants are the Carboniferous and Permian basement rocks, as revealed by the U-Pb single zircon ages of the inherited crystals. The DM model Hf ages of inherited zircons and zircons from the basement rocks cluster around 900 Ma.

Chronological history of UHP rocks from the Chinese Continental Scientific Drilling: A multi-methodical approach

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Ultrahigh pressure (UHP) rocks from the Chinese Continental Scientific Drilling (CCSD) program were chosen to study the Sm-Nd and Lu-Hf isotope systems in combination with U-Pb LA-ICP-MS and SHRIMP dating of distinct zircon domains. Comprehensive studies of the different lithologies on various sections of the drill hole should provide a better understanding of the metamorphic evolution of the Sulu terrane. Additionally, our multi-methodical approach provides the opportunity to compare the different chronometers and test their robustness and limitations (e.g. mineral inclusions, incomplete equilibration, resetting). Multistage zircon growth can be observed in most Sulu-Dabie UHP rocks. Inherited and metamorphic zircons were distinguished on the basis of transmitted light microscopy, cathodoluminescence (CL) imaging, trace element contents, Hf isotope composition and mineral inclusions. Inherited zircon of middle Neoproterozoic age have variable trace element pattern that are considerably different from that of metamorphic zircon domains. Based on CL, mineral inclusion and U-Pb ages up to three phases of Triassic zircon growth or re-crystallisation can be identified in a single sample. The ages are interpreted to date the time of (1) prograde and (2) UHP metamorphism during subduction, and (3) later retrograde metamorphism during exhumation.

Metamorphic domains from a single sample have commonly a uniform Hf isotope composition indicating isotope equilibration in the decimetre-scale during the Triassic UHP event. This composition varies between different samples and is generally significantly more radiogenic than that of the inherited cores and thus the bulk rock. Its respective value is controlled by the percentage of dissolved or re-crystallized inherited zircon, with low Lu/Hf and relatively unradiogenic $^{176}Hf/^{177}Hf$, and the bulk rock composition.

Analyses of the Lu-Hf and Sm-Nd system of mineral separates (garnet, clinopyroxene …) are currently in progress. According to SHRIMP and LA-ICP-MS U-Pb ages of metamorphic zircon from the same and various other UHP rocks ([1-3] and references therein) lasted the metamorphic evolution of the Sulu-Dabie terrane around 30 Myr, with about 20 Myr of HP or UHP metamorphism.

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Dynamics and longevity of the magmatic system of Furnas volcano, São Miguel, Azores

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Furnas is the easternmost of the three active trachytic central volcanoes on the island of São Miguel, Azores. It is regarded as one of the most active and dangerous volcanoes in the Azores archipelago owing to a population of several thousand people living within the caldera and in the immediate vicinity of the volcanic complex. Throughout its history, volcanic activity at Furnas has been essentially explosive but eruptive styles have varied from mild effusive activity to at least two caldera-forming eruptions ~30,000 and 12,000-10,000 years BP [1].

During the past 5,000 years, ten explosive eruptions occurred at Furnas, which produced a total of ~0.9 km^3 (DRE) of fairly homogeneous trachytic magma. The deposits of these eruptions are collectively referred to as Furnas A-J members of the Upper Furnas Group [1,2]. The latest eruption (Furnas J) occurred after the settlement of the Azores archipelago in 1630 AD. Eruptions of the Upper Furnas Group were mainly characterised by alternating episodes of magmatic and phreatomagmatic activity producing deposits of interbedded ash and lapilli that overlie the widespread Fogo A deposit from adjacent Fogo volcano [3]. At least three of these eruptions, namely Furnas E, Furnas I and the 1630 AD event (Furnas J), were accompanied by trachyte dome extrusion in the final phases of the eruption [3].

To develop a fuller understanding of the underlying dynamics of the magma system of Furnas, we have investigated the whole-rock major and trace element geochemistry of the products of the Upper Furnas Group and the older caldera-forming events. These data are discussed together with U-Th-Ra isotopic disequilibria obtained on trachyte pumice clasts and lavas to place constraints on the dynamics and longevity of the magma system of Furnas.

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Designing a dissimilatory iron reducer. Reconstitution of the Fe(III)-reducing electron transport chain of *Shewanella oneidensis* MR-1 in *Escherichia coli*

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Shewanella oneidensis uses several electron acceptors to support anaerobic respiration including soluble species and remarkably insoluble species such as iron(III) and manganese(IV) oxides. The pathway of electron flow from the cytoplasmic membrane to the outer membrane remains elusive after years of research with different *Shewanella* species. We are pursuing a novel approach to identify the essential components of the electron transport chain by reconstituting the pathway for iron(III) reduction by *S. oneidensis* in *Escherichia coli*. We generated a suitable *E. coli* strain as a platform for this work and integrated the central electron transfer protein, CymA into the genome. CymA allows for electron transfer from the cytoplasmic membrane to the periplasmic space in *Shewanella* species. We showed (i) that the expressed CymA activity is growth supporting for *E. coli*, (ii) that CymA couples directly to the soluble fumarate reductase of *S. oneidensis*, and (iii) that CymA in vitro facilitates reduction of ferric citrate and the soluble quinone analog AQDS. Our generated *E. coli* strain is a dissimilatory iron reducer in that it can use ferric-NTA as a terminal electron acceptor during growth with glycerol as the sole carbon and electron source. We could furthermore show through in vitro assays that a direct interaction between CymA and the periplasmic decaheme cytochrome MtrA from *S. oneidensis* is possible.

Magma mixing and mingling textures and geochemistry of microgranular enclaves in granitoids of SE Semnan, N Iran

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Discussion

Many granitoid intrusions display textural and geochemical evidence for the intraction of mafic and silisic magmas during their genesis [1]. The post-middle Eocene granitoids from SE Semnan, N Iran have many fine grained mafic microgranular enclaves, with diameters between 1 to 15 cm. Their composition varies from monzonite, quartzmonzodiorite – monzodiorite and monzogabbro – and exhibites evidence for magma mixing and mingling both at outcrop and at thin sections. These textures are antirapakivi feldespare, acicular and prismatic apatites, inclusion of mafic zones in feldspares, spongy cellular plagioclase, reverse zoning in plagioclases and etc.. In host granitoid rocks there are also two types of biotites in composition (that one types have high TiO_2, Al_2O_3 , MgO and low SiO_2, are similar to contents of these elements in mafic microgranular enclaves and second types are depleted in TiO_2, MgO and enriched in Al_2O_3 and SiO_2) and reverse plagioclases zoned. The magmatic origin of enclaves is suggested by their typical igneous textures, such as with abundant acicular apatite, elongate zircon, the euhedral form of the mafic phases, porphyritic texture and plagioclase zoned [2]. These observations suggest that the mafic microgranular enclaves are derived from a hybrid magma formed as a result of the intrusion of mafic magma into the base of a felsic magma chamber.

Conclusions

The mafic microgranular enclaves have igneous mineralogy and textures. The petrographic, chemistry of minerals and whole-rock geochemical relations, in the mafic microgranular enclaves and their host rocks, indicate that magma mixing and mingling played a important role during their evolution .

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Carbonate clumped isotope thermometry of molluscs and its applications to Pleistocene gastropod fossils from South Dakota

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Ghosh *et al.*, (2006) [1] present a carbonate clumped isotope palaeo-thermometer. Otolith aragonite from fishes collected over a range of known temperatures [2] validates the original calibration of this thermometer for inorganic calcite precipitate (ICP) and coralline aragonite [1]. Here we present a calibration for molluscs, including gastropods collected from nature and inferred to have grown at widely different temperatures (2-25°C). The growth temperatures for these samples were estimated based on mean annual temperature (MAT) at the site of collection. We speculate that these growth temperature estimates could be biased by unknown and possibly variable amounts to due seasonality of growth and/or other factors. Despite these uncertainties, the mean trend in the relationship between inferred growth temperature and $^{13}C^{18}O^{16}O$ content of CO_2 extracted from mollusks is indistinguishable from that previously documented for ICP. The proportionality for molluscs can be described between 1 and 25 °C by the function: $\Delta_{47} = 0.0603.10^6 \cdot T^{-2}$ -0.0496, where Δ_{47} is the enrichment, in per mil, of $^{13}C^{18}O^{16}O$ in CO_2 relative to the amount expected for a stochastic (random) distribution of isotopes among all CO_2 isotopologues [3,4], and T is the temperature in Kelvin. However, due to scatter in these new data, we suggest that the statistically indistinguishable and more precisely known trend for ICP should be used for molluscs.

We apply the carbonate clumped isotope thermometer to gastropods (*Physella*) deposited concurrently with mammoth skeletons in a sinkhole deposit in South Dakota, USA. The age of deposition of the analyzed samples was 26,075±880 years BP, based on ^{14}C dates for bone apatite collected from the same strata [5]. We analyzed aragonite powder from 15 *Physella* shells collected from various depths across a 255 cm vertical section from this location. Our results provide an estimate of 31.2±3.34°C for the average temperature of water at the time of deposition. The average $\delta^{18}O$ value of sinkhole water was (calculated assuming an equilibrium fractionation of ^{18}O between carbonate and water [6]) -10.5±0.66‰. We estimated MAT using a combination of modern day MAT and $\delta^{18}O$ of rainfall from the same area. Our results suggest that the average temperature in the area was 4.3°C colder at the time of deposition than it is today.

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Isotopic composition of methane and ΣCO_2 from Arsenic affected area of West Bengal, India

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Ground water is a potential source of methane (CH_4) in Arsenic affected area of Bengal Basin. Harvey *et al.* (2002) observed high CH_4 concentration in the water with high As abundances at depth and predicted increase in CH_4 concentration during dry seasons. We present our study on tube well water samples collected during dry season (middle of February 2007) from two different localities in West Bengal, belonging to two different palaeodrainage systems i.e. Bhagirathi Ganges delta (BL) and Damodar river fan delta (BG) (tributary of river Bhagirathi) (Acharyya and Shah, 2007). Many of these wells were previously studied for As concentration (Acharyya and Shah, 2007).

CH_4 and ΣCO_2 present in the water samples were analyzed for carbon isotopic ratios to trace the sources of carbon to the ground water. Most of the samples analyzed for ΣCO_2 in this study have $\delta^{13}C$ in the range -10.8‰ to -13.5‰, suggesting that the CO_2 in these samples originate from silicate weathering with CO_2 from vegetation (C_3 type). Barring one sample, we saw two distinct clusters of $\delta^{13}C$ values in CH_4: -74.9 ‰ to -87.5 ‰ for BL water compared to a range of -30.5 to -40.2 ‰ in BG water. Isotopic signatures suggest a predominance of the carbonate reduction pathway in BL sites and high activity of CH_4 oxidation or substrata depletion in BG sites. Our preliminary results suggest that the process of release of arsenic from hydrated iron oxide is triggered by the activities of anaerobic bacteria in a reducing environment with consequent production of CH_4 with distinctly depleted isotopic character.

We also observed an anomalous enrichment of $\delta^{13}C$ value (+55 per mil) in one of the samples with low CH_4 concentration from BL locality.

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Nanoscale size effects on reduction of hematite nanoparticles and surface reactions of Uranium(VI)

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The high surface area to mass ratios of hematite nanoparticles can increase the extents of surface reactions that affects the environmental biogeochemistry of pristine and contaminanted environments. Surface reactions of interest include adsorption and surface-mediated reduction. Microbial iron reduction can produce Fe(II), which, when adsorbed to Fe(III) oxides, is an effective reductant of contaminants including uranium(VI). In order to understand nanoscale effects on the rate of microbial iron reduction and surface-mediated uranium(VI) reduction, hematite nanoparticles with diameters of 8, 50, and 200 nm were synthesized using gas phase methods that provide control of their composition and sizes.

The microbially-mediated rate of hematite reduction by the iron-reducing bacteria *Geobacter sulfurreducens* has been studied in anaerobic batch experiments. Abiotic reductive dissolution rates using ascorbic acid and the reduced form of the electron shuttle AQDS have also been studied. The dissolution rates increase with decreasing particle size; however, when normalized to surface area, the dissolution rates are similar for all but a few conditions.

Uranium(VI) adsorption to the three sizes of hematite particles was evaluated over the range of pH (3-11) and total uranium concentration (10^{-6} to 10^{-4} M) to elucidate the size dependence of U(VI) adsorption to hematite. All experiments were conducted in a CO_2-suppressed glovebox to prevent the formation of dissolved U(VI)-carbonate complexes, which can affect U(VI) adsorption. Surface complexation modeling was used to provide a quantitative reaction-based framework for evaluating the effects of particle size on adsorption. A model was developed that can predict U(VI) adsorption over a range of pH values and total U(VI) loadings.

Rates of U(VI) reduction by adsorbed Fe(II) were investigated in batch experiments. Reduction is interpreted as a pseudo-first-order reaction with respect to the activity of the adsorbed U(VI) with an excess of Fe(II) relative to U(VI). At each sampling time, a portion of the suspension was filtered and analyzed for dissolved iron and uranium using ICP-MS. Additional portions of the suspension were chemically treated for the extraction of total U(VI) and Fe(II). Selective extraction of U(VI) uses 0.1 M $NaHCO_3$ while that of Fe(II) uses 0.5 M HCl. The concentration of Fe(II) was subsequently measured using the ferrozine method.

Tracking CO₂ leakage with noble gases

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The geological storage of greenhouse gases such as CO_2 in saline aquifers is an active research topic. By this way, effects of these gases on the environment may be significantly reduced. One limiting parameter of this type of storage is actually the hypothetical CO_2 leakage through the caprocks. Some studies of natural CO_2 gas fields have shown that noble gases are able to trace CO_2 origins and physical processes which have occurred in the subsurface (Gilfillan, 2006). Unfortunately, the migration of noble gases through low permeability media is still poorly constrained.

Here, we describe experimental results concerning the diffusion of gases through different porous clayey media. The experimental setup is a diffusion reactor composed of two gas reservoirs separated by a water saturated clay membrane. Initially, one side is filled with CO_2 mixed with trace amounts of noble gases (He, Ne, Ar, Kr and Xe), the other side is filled with pure oxygen to equilibrate pressures on both sides of the membrane.

Unexpectedly, diffusion of CO_2 is faster than those of He and any of the other noble gases. This result points to the effect of the solubility in the migration process, allowing CO_2 to migrate faster as it is highly soluble in water. In addition, in clay rocks, the "bound water" plays a role in this migration because solubility and diffusion factors contrast with those associated with "free water". We used a 2D diffusion model at the pore scale (Kara, 2004) to determine diffusion and partition coefficients of noble gases between free and bound water as a function of petrographical parameters (mineralogy, porosity, tortuosity). The behavior of noble gases during a diffusion process will be presented in order to highlight the main parameters likely to control their migration.

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A δ¹³C depth gradient from a mid-Cryogenian platform margin: Evidence for Neoproterozoic ocean stratification

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A $\delta^{13}C$ depth gradient of at least 8‰ between shallow and deep water is evident in Neoproterozoic carbonates from the Umberatana Group in the northern Adelaide Fold Belt, South Australia. The progradation of an extensive mid-Cryogenian platform margin allows direct isotopic comparison between shallow-water reef carbonates and synchronous deep-water slope and basinal sediments. With over 1 km of relief this platform margin allows an estimation of seawater $\delta^{13}C$ in the upper 1000-1400 m of the water column.

We suggest that the observed $\delta^{13}C$ gradient is the result of poor ocean circulation brought about by salinity stratification that persisted at least for the progradational history of the Oodnaminta platform margin. Such conditions enhanced the effect of the 'biological pump' by drawing ^{12}C out of the surface ocean and accumulating it in the deep ocean. After prolonged stratification, the vertical $\delta^{13}C$ gradient increased to the observed magnitude.

Furthermore, we propose that stratification was persistent throughout Neoproterozoic time, and can explain many of the unusual features that characterise this era – large-scale $\delta^{13}C$ variation, extreme climatic fluctuations, and the presence of cap carbonates. Stratification creates an unstable climate system in which gradual accumulation of CO_2 in deep waters eventually leads to global glaciation due to the lack of deep ocean ventilation. Subtle changes in ocean circulation ventilate the deep ocean and rapidly transfer large amounts of CO_2 to the surface ocean and atmospheric reservoirs, leading to greenhouse temperatures, and facilitating rapid global deglaciation and cap carbonate deposition. Additionally, oxygen accumulated in the surface ocean and atmosphere during prolonged periods of stratification may have triggered the evolution of the Ediacaran fauna during the terminal Neoproterozoic.

The results also imply that the use of carbon isotope chemostratigraphy as a high-resolution chronostratigraphic correlation technique for the Neoproterozoic may be invalidated by evidence for strong facies-dependant $\delta^{13}C$ variation.

Metal sulfates in PM emissions from a coal-fired power plant

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Coal combustion facilities represent a major source of fine particulate matter (PM) in the atmosphere. The particle-capture efficiency of air pollution control devices is size-dependent, and is considerably lower for particles with diameters <2.5 micrometers ($PM_{2.5}$) than for larger ones. These particles are thus emitted preferentially and, moreover, exhibit relatively long atmospheric residence times. To assess the environmental and health impacts of such PM, it is necessary to obtain information about its mineralogical composition.

We report results from SEM, TEM and XRD investigations on PM emitted from a stoker boiler. The samples, collected on filters placed in the smokestack above all air pollution control devices, represent PM that would have escaped into the atmosphere. Our study demonstrates that these fugitive particles in the $PM_{2.5}$ fraction consist of amorphous material (Al-Si-glass, soot, native Se) and a variety of crystalline phases, including lime, mullite, and various euhedral metal sulfates. Electron diffraction patterns and chemical compositions obtained by quantitative analytical TEM revealed the presence in the PM of the following sulfates (Gieré *et al.* 2006): anglesite ($PbSO_4$) as main host of Pb; anhydrite ($CaSO_4$); gunningite ($ZnSO_4 \cdot H_2O$); and yavapaiite ($KFe(SO_4)_2$), a mineral that is exceedingly rare in the geosphere. In the larger size fraction, we have identified the following additional phases: voltaite and zincovoltaite - $K_2(Fe^{2+},Zn)_5(Fe^{3+},Al)_4(SO_4)_{12} \cdot 18H_2O$, millosevichite - $Al_2(SO_4)_3$, meta-aluminite - $Al_2(SO_4)(OH)_4 \cdot 5H_2O$, and tamarugite - $NaAl(SO_4)_2 \cdot 6H_2O$.

It is concluded that most of these metal sulfates were precipitated from the flue gas, that large quantities of these phases may be emitted globally into the atmosphere through combustion processes, and that they have, through hydration and dissolution, a major environmental and health impact.

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Comparative apatite fission track study of conventionally versus selFrag Lab fragmented samples

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Geochronological dating methods like apatite fission track analysis require an efficient liberation of single mineral grains for analysis. The selFrag Lab machine (produced by Amman AG, Langenthal, Switzerland) disaggregates geological materials by releasing short pulsed high-voltage discharges to an in water immersed sample. The produced, fast-expanding plasma channel induces shockwaves, similar to an explosion, that propagate through the sample. Refraction at discontinuities like grain boundaries, crystal internal surfaces or fluid inclusion trails results in selective break-up of the aggregate, yielding natural shaped homogeneous grains (Gnos *et al.*, 2006 and references therein). However the HV-discharge may also produce local temperature peaks of up to 10'000°C of very short duration within the narrow plasma channel. Does this heat production affects fission tracks in apatite? Test were conducted to control whether this very localized heat production leads to partial fission track annealing starting at approximately 60°C. Prolonged exposure to temperatures exceeding 110°C would result in a complete reset of the apatite fission track record. Hence, any temperature impact on the apatite during processing could change the resulting fission track data.

Therefore a comparative study using two different samples, prepared by conventional and selFrag Lab processing, has been performed in order to investigate a possible influence of the selFrag Lab disaggregation method on apatite fission tracks.

Both investigated samples, a granitoid gneiss from Madagascar, and the Fish Canyon Tuff, a frequently used age standard in geochronology, yield statistically identical track length distributions when comparing conventional and selFrag Lab separation methods. This study yields a first confirmation that selFrag Lab processing does not cause annealing under the applied machine settings and seems to provide an alternative method for rock disaggregation for apatite fission track analysis.

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Surface and electronic structure effects on interfacial charge transfer at iron oxide nanoparticle surfaces

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Transition metal oxides and oxyhydroxides form important reactive nanomaterials in certain terrestrial environments. There is considerable interest in defining and understanding nanoparticle reactivity with respect to (bio)geochemical processes, but the task is challenging due to the complex interplay of structural and chemical properties in nanoscale solids. Iron oxide and oxyhydroxide nanoparticles are of particular importance, participating in redox cycles driven by (bio)geochemical processes including inorganic precipitation, (photo)reduction and microbial metabolism. The reductive dissolution of such nanoparticles is an important link between biological and mineral geochemistry. For example, dissimilatory iron reducing bacteria use fine grain iron oxyhydroxide nanoparticles as terminal electron acceptors during anaerobic carbon respiration. Interfacial electron transfer is a key step in such reductive transformations, and is highly sensitive to the interaction between the electron donor and the surface and electronic structure of the substrate.

Soft x-ray spectroscopy can reveal the electronic structure of semiconductor minerals [1] and nanoparticles [2] and is anticipated to be a versatile method for predicting the thermodynamic basis of charge transfer at nanoparticle surfaces. Nanoscale iron oxide and oxyhydroxide nanoparticles exhibit modified electronic structure [2] that would alter the ability of surface adsorbed electron donors to drive reductive dissolution. However, aqueous chemistry studies that attempt to validate these predictions are difficult to interpret on the basis of the x-ray spectroscopy data alone.

We discuss ways to distinguish (i) the thermodynamic and kinetic controls on iron oxide nanoparticle reduction and (ii) the electronic and structural causes of modified reactivity. Optical and infrared spectroscopy do not detect differences in the binding of bidentate organic ligands to iron oxide bulk and nanoparticle surfaces, suggesting a minor effect of modified surface structure. However, deviations from the anticipated the pH-dependence of photoreactivity [3] suggests there may be considerable heterogeneity in nanoparticle redox behavior.

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Phosphoric acid fractionation factors for aragonite between 25 and 72°C with implications on aragonite-calcite oxygen isotope fractionation

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We determined the intramolecular kinetic oxygen isotope fractionation between CO_2 and CO_3^{2-} during reaction of phosphoric acid with aragonite and calcite between 25 and 72°C. We analyzed clear single aragonite crystals from Bilina (Czech Republic), Leogang (Austria), and Agrigento (Italy), a fine-grained coralliform aggregate from the Styrian Erzberg (Austria), and for comparison calcite NBS-19. The aragonites show a wide range of total oxygen isotope values from 17.5 to 39.5‰ (VSMOW). Our result for NBS-19 (28.76‰ VSMOW) is within 0.12‰ of the recommended value.

The oxygen isotope fractionation between acid-liberated CO_2 and aragonite at 25°C expressed as a 1000lnα value is consistent for our samples with 11.14 ±0.20‰ (n=4). Our new value is significantly larger than the commonly applied values of 10.34 or 10.20 (Sharma and Clayton, 1965) and our new value for calcite NBS-19 (10.08‰), but is similar to those of synthesized aragonite reported by Kim and O'Neil (1997). At temperatures between 25 and 72°C, the phosphoric acid fractionation (PAF) of aragonite can be expressed as:

$$1000ln\alpha^{PAF}_{aragonite} = 5.32*(1000/T[K]) + 5.07$$

Our results imply that the published equilibrium $^{18}O/^{16}O$ fractionation factors between aragonite and water (e.g. Kim *et al*. 2006) need to be revised. Considering our new acid fractionation factors, oxygen isotope fractionation between aragonite and calcite is very small (<0.2‰) as suggested by recent theoretical calculations (Schäuble *et al*. 2006).

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Geothermometry of oxidized Zn-Pb ores: Oxygen isotope systematics and a new femtosecond laser technique on monophase fluid inclusions

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We studied the $^{18}O/^{16}O$ systematics of carbonate minerals from supergene oxidized Zn-Pb deposits and from submarine alteration of ancient slags to constrain oxygen isotope fractionation factors for smithsonite, cerussite, and phosgenite. The temperature dependence of oxygen isotope fractionation between Pb and Zn carbonate minerals and water below 100°C can be expressed as

$$1000 \ln\alpha_{cerussite\text{-}water} = 2.29\,(10^6/T[K]^2) - 3.56$$
$$1000 \ln\alpha_{smithsonite\text{-}water} = 3.10\,(10^6/T[K]^2) - 3.50$$
$$1000 \ln\alpha_{phosgenite\text{-}water} = 2.55\,(10^6/T[K]^2) - 3.50$$

Average formation temperatures of the studied supergene deposits (SW Sardinia, E Belgium, Broken Hill district, Australia, and others) are calculated to be 20 ± 5°C using the estimated isotope compositions of local paleometeoric waters.

We also applied a new technique using a femtosecond laser to nucleate the vapor bubble in monophase fluid inclusions. Homogenization temperatures of inclusions in cerussite and hemimorphite from the same deposits range from +6.1 to +25.5°C and confirm our stable isotope results.

New fluid inclusion and oxygen isotope data from willemite-bearing oxidized Pb-Zn ores from E Belgium and S Portugal, however, suggest that certain mineralization stages in these districts were formed by distinct low-temperature (<50°C) hydrothermal systems involving saline fluids.

Thus, oxygen isotope and fluid inclusion data for base metal carbonate minerals can be used to distinguish ores produced by weathering from very-low-temperature hydrothermal ores. They may also provide valuable paleoclimatic information.

Organic geochemical assessment of the onset of an Oceanic Anoxic Event

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A geochemical study was conducted on cored Posidonia Shale sections and underlying sediments derived from two wells located in the southern North Sea offshore the Netherlands. Samples were subjected to a variety of analytical techniques including CS analysis, Rock Eval pyrolysis, GC-MS and carbon and sulphur isotope analysis. It is well established that the Posidonia Shale (Early Toarcian) is marked by the deposition of organic-rich shales throughout Europe as a result of an Oceanic Anoxic Event (OAE). Our data provides evidence that establishment of these anoxic conditions is a gradual process from sediment anoxic conditions into true anoxia within the Posidonia Shale. This is indicated by the depth profile of most of the measured parameters. The values of sulphur content, TOC, hydrogen index, Ts/Tm ratio and pristane/phytane ratio gradually increase in the underlying sediments with decreasing depth towards the Posidonia Shale. Within the Posidonia Shale the values of those parameters remain constant.

The carbon isotope data show a negative excursion within the Posidonia, in agreement with earlier reports. This indicates that OAE might have been a global event. Our research focuses, among others, on the question whether this proto OAE development can be recognised throughout the basin.
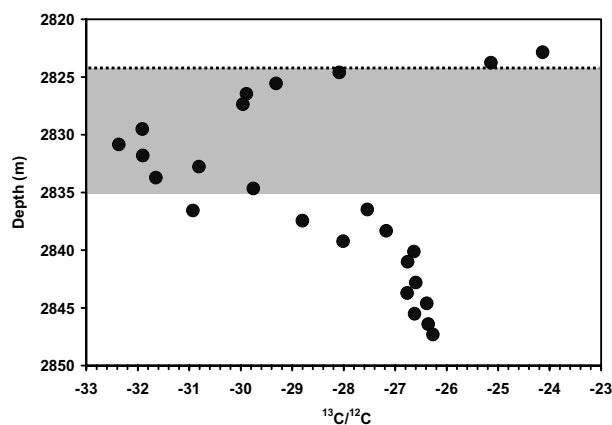

Figure 1: Illustration of the carbon isotope excursion (approximately 7 ‰) in the Posidonia Shale(shaded region)

Oceanic hornfels: Records of heat transport near axial magma chamber roofs

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The transfer of heat from the lower to upper ocean crust is the most fundamental process shaping the morphology of mid-ocean ridges and determining the mechanism of accretion of the lower crust. At fast-spreading mid-ocean ridges, the heat that drives high temperature hydrothermal systems is focused at the top of axial magma chambers (AMCs) that reside 1–2 km beneath the seafloor. Theoretical models predict that heat is exchanged across thin (<100 m), hot (>650°C), impermeable conductive boundary layers (CBLs) sandwiched between AMCs and permeable upper crust. The thickness of the CBL is predicted to vary with time, in response to magmatic activity and would have a finite life that is dependent upon the longevity of an AMC. Thus, CBLs are not static features, but rather should vary in thickness and position, depending on the magma supply and frequency of diking. While conceptually robust, there is sparse evidence in support of these predictions, perhaps because CBLs are transient and short-lived, thus preventing their preservation.

The expected characteristics for CBLs were recognized within *hornfelsic* dikes found within a contact aureole at the base of the sheeted dike complex in the Troodos opholite (Gillis and Roberts, 1999), and dikes intruding the uppermost gabbros in the Oman opholite and two regionally extensive tectonic escarpments of young fast-spreading East Pacific Rise crust exposed at Pito and Hess Deeps. These very fine-grained, granoblastic hornfels occur either as *in situ* dikes or xenoliths in the gabbro sequence. Where *in situ*, they form massive, indurated outcrops that lack the common ladder-like fracture patterns of sheeted dikes. Hydrothermally altered dikes are partially to completely recrystallized to pyroxene and/or hornblende hornfels, recording episodes of re-heating at 750–1050°C. Field relationships and temperture constraints indicate that the heat flux across the CBLs is 12–33 Wm^{-2}, similar to the latent heat of crystallization released to build a vertical thickness of 6 km crust. These are also similar to normalized values for hydrothermal plumes (20–40 MW/km), indicating that the heat that drives hydrothermal convection is transferred across a conductive boundary layer.

Collectively, widespread distribution of hornfelsic dikes at or just below the sheeted dike – gabbro transition indicate that thermally metamorphosed rocks are common feature in ocean crust. I will argue that these thermally metamorphosed rocks are remnants of preserved CBLs that record the migration of magma–hydrothermal boundaries, thus providing tangible evidence for AMC dynamics.

Assimilation of the plutonic roots of the Andean arc: Evidence from CO_2-rich fluid inclusions in olivines

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Assimilation of young plutonic rocks by magmas of similar compositions is not easily seen in isotopic signatures because of their low isotopic contrast with the magmas. However, variability of trace element ratios in Tatara-San Pedro basalts (SVZ of the Andes) suggests assimilation (Dungan *et al*., 2001). Mineral inclusions and healed microfractures (HMF, Dungan and Davidson, 2004) show the xenocrystic nature of their crystals.

We compare olivine xenocrysts from a basaltic unit with amphibole- and phlogopite-bearing gabbroic xenoliths from a Holocene dacite (Costa *et al*., 2002) and analyse the contents of their HMFs using SEM, electron microprobe, Raman spectroscopy, microthermometry and LA-ICP-MS.

The better preserved fluid inclusions and textures in xenoliths reflect interactions between CO_2-rich, saline H_2O-bearing fluids and gabbroic intrusions. This subsolidus history then influences the partial melting and assimilation of the gabbros at the contact of the dacite host. The presence of hydrous minerals, especially micas, favours melting even at moderate magmatic temperatures.

In olivine xenocrysts from the basaltic units, most of the healed microfractures have been reopened upon ascent or eruption, thereby partly destroying the subsolidus signal. Diffusion modeling on iron-rich zones along the HMFs give a very short residence times (a few hours) suggesting syn- or post-eruptive healing. This is easily explained by the higher temperature of the basaltic host compared to the dacite. However some fluid inclusions are preserved and their similarity with those found in the xenoliths suggests similar origins for the xenocrysts.

Distinct mineralogical assemblages between xenocrysts-bearing basalts (olivine + plagioclase + clinopyroxene) and the gabbroic xenoliths (lacking clinopyroxene) show the diversity of the plutonic crust that was sampled by these magmas. Variable amounts of micas and amphiboles in the original gabbro will influence the chemical effect of assimilation on the bullk rock chemistry of the host magma.

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Proton and lead adsorption onto roots of the grass species *Festuca rubra*

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Metal adsorption onto biological surfaces can significantly affect metal speciation and mobility in near-surface environments. Cell wall adsorption, whether involving bacterial or root cells, is likely the first step in nutient acquisition, but can affect the distribution of heavy metals and radionuclides as well. Many previous studies have focused on bacterial cell wall adsorption. However, plant roots can adsorb a range of metals as well. Quantifying metal adsorption onto plant root surfaces will assist in understanding the speciation of metals in complex soil systems, and can provide insights into how plants compete with soil bacteria for metal nutrients.

In this study, we measured proton and Pb binding onto roots of *Festuca rubra*, a species of grass commonly referred to as red fescue. Potentiometric titrations were performed on washed root material, using 0.1 M $NaClO_4$ to buffer ionic strength. Like bacteria, the roots exhibited continuous buffering behavior from pH 3 to 9. We use a discrete-site non-electrostatic surface complexation model (SCM) to constrain acidity constants and concentrations for root cell wall functional groups from the titration data. The Pb adsorption experiments were conducted at fixed Pb and root concentrations, with fixed ionic strength, as a function of pH. The roots displayed a typical adsorption edge, with the extent of adsorption increasing with increasing pH, and we use the Pb adsorption data to constrain the values of the thermodynamic stability constants for the important Pb-root surface complexes.

Our results indicate that the cell wall material associated with *F. rubra* roots has a different functional group chemistry than the cell wall material associated with bacteria. Nevertheless, plants and bacteria show a similar overall ability to uptake metals. We use the modeling results from this study to estimate Pb distributions in realistic soil systems containing root material, bacterial cells, and mineral surfaces, and we demonstrate that each reservoir can be important in determining the distribution of Pb in soil settings.

Direct evidence of the feedback between climate and weathering

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The major long term climate moderating process on the surface of the Earth is the link between climate and chemical weathering through the greenhouse effect; the higher the temperature, the faster the weathering rate and CO_2 sequestration. Weathering releases divalent cations to the ocean via riverine transport, either in dissolved and suspended form, where they promote the drawdown of CO_2 from the atmosphere by carbonate mineral precipitation (e.g. Walker *et al.*1981; Gislason *et al.* 2006). To test this widely held hypothesis, we performed a field study determining the weathering rates of 8 Icelandic watersheds over the past 40 years. The annual average temperature of individual watersheds increased by 0.4 to 1.4 °C. Precipitation increased or decreased depending on the catchment. Riverine transport of weathering products from each watershed has continuously increased. The increase in dissolved riverine inorganic carbon and calcium transport range from less than one percent to 70 percent for the period 1960 to 2000. The riverine suspended inorganic particulate matter in the same catchments for the same period has increased by 2 – 600 percent. These results clearly indicate 1) the strong feedback between climate and Earth surface weathering, and 2) that the climate moderating effect of weathering, and therefore atmospheric CO_2 sequestration, may be far faster than previously thought.

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The sedimentation rate controls microfossil preservation

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One of the greatest challenges to finding definitive evidence for life on early Earth is the discovery of well preserved fossils. The microscopic, soft bodied organisms that are expected to dominate early or extreme environments do not preserve well. Several laboratory studies have recreated microbial "fossils" [1, 2], but the conditions under which microfossils are formed in natural environments are still poorly understood. Knowing these conditions and being able to predict where they occur are key factors to discovering preserved microorganisms. Exposure to iron in particular appears to control the formation of microfossils in many terrestrial and marine environments [3].

We present new data from oolitic ironstones at the Callovian-Oxfordian boundary in the eastern Jura mountains of northern Switzerland linking the preservation of fossil microorganisms to the depositional environment and to the concentration of iron. The lowest Oxfordian deposits contain litho- and bioclasts, which are indicative of a highly condensed sequence with reworking and a sedimentation hiatus. In this sequence, filamentous, tubular structures of 1-2 μm are found in ferriferous encrustations and goethitic ooids. The filaments appear identical to those formed by a recently characterized modern analog, the NO_3- reducing, iron-oxidizing bacteria. Depositional sequences from the upper Callovian stage exhibiting a higher sedimentation rate do not contain the same structures. We hypothesize that 1) the activities of iron-oxidizing and -reducing bacteria contributed to the form of iron that was accumulated and 2) a hiatus in sedimentation during development of the sequence enabled the microbial structures to be preserved. In contrast, when the sedimentation rate was increased, the burial of the microorganisms facilitated the breakdown of their associated structures. We suggest that this environment provides a model system for establishing the relationship between sedimentation and the preservation of soft bodied, microscopic organisms.

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Single crystal X-ray refinement and thermodynamic properties of stoichiometric jarosite, $KFe_3(SO_4)_2(OH)_6$

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Jarosite and related minerals are invariably found in natural environments acidified either through the action of acid rain or by acidic mine drainage. In spite of their importance and common occurrence, the data which could describe the solubility, precipitation, and distribution of elements beetwen jarosite and aqueos solutions are fragmented or questionable.

The first goal of this study is to prepare stoichiometric jarosite samples for further thermodynamic investigation. We have synthesized only jarosite samples which have been prepared according to the published procedures (Grohol *et al*., 2000) by oxidizing metallic iron in acidic K^+ and SO_4^{2-}-containing solutions under hydrothermal conditions. Iron was addedin the form of an iron wire. Synthesis was carried out in a Teflon cylinder placed into a conventional oven at 200°C. The yellow product was readily identified by X-ray diffraction (XRD) as jarosite and no other crystalline phases were detected. The yield of the synthesis was 230 mg. The single-crystal XRD refinement for the sample with R_1=0.0316 for the unique observed reflections ($|F_o| > 4\sigma_F$) and wR_2=0.0423 for all data gave the unit-cell parameters a = 7.288(1) and c = 17.203(4) Å. The Fe site occupancy in this sample is 97(1) %., significantly higher than the ~85 % reported from a conventional synthesis routes.

The second goal of this study is to determine thermodynamic properties of the jarosite sample. The thermodynamic measurement will be carried out using acid-solution calorimetry to obtain the enthalpy of formation. Heat capacity and entropy at standard temperature and pressure will be measured by adiabatic calorimetry. The measured enthalpy and entropy will be combined to a Gibbs free energy of formation. Then we will proceed to refine the existing values by comparing them to phase equilibria data, either in nature or laboratory.

The data which will be presented can be used to calculate phase diagrams for this group of phases at conditions relevant to low-temperature geochemical processes (25 °C, 1 bar), metallurgical treatment (75 – 110 °C), and stability of phases on the surface of planets.

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In situ redox chemistry of hydrothermal fluids at the Loihi Seamount Microbial Observatory

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Loihi Seamount is a submarine, active volcano located on the southeast flanks of the Big Island of Hawaii. It is considered to be the youngest volcano in the Hawaiian chain, sharing the hot spot magma chamber with Mauna Loa and Kilauea. Sites of both vigorous and diffuse hydrothermal venting can be found surrounding the pit crater summit (~1000m) and on the flanks of the seamount, down to its base (~5000m). Vent fluids at Loihi are chemically distinct from other well-studied marine hydrothermal systems and have been shown to be enriched in carbon dioxide, iron(II), and manganese(II), and deplete in sulfur species. The Loihi summit is located within a zone of low oxygen, further enabling elevated iron(II) concentrations and support for a dominant community of iron-oxidizing bacteria.

We deployed a combination of a sensor wand consisting of up to four voltammetric working electrodes and the ROV Jason temperature probe, and/or a submersible micromanipulator with voltammetric electrodes to provide real time in situ redox characterizations of hydrothermal fluids and geochemical gradients associated with iron-oxidizing microbial mats and flocs. Our in situ electrochemical analyses provided an efficient and valuable means for directed discrete sampling of hydrothermal fluids and microbial flocs, as well as previously unattainable high spatial resolution geochemical profiles through the mats.

Automated fission track dating of apatite and monazite by image analysis and ICP-MS

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The microscopic identification and counting of fission-tracks in accessory minerals by a manual observer has been a significant limitation to the widespread adoption of fission track dating (FTD). Manual counting methods require a high level of observer skill and calibration, and provides a practical limit to the number of tracks counted and hence on the precision achieved. It has long been hoped that automated methods for track recognition and counting could enhance the objectivity of fission-track analysis, and improve both precision and overall productivity. We have recently developed a new image analysis method, called *'Coincidence Mapping*[TM]*'* that for the first time shows great promise in achieving these aims.

Another limitation in traditional FTD arises from the use of thermal neutron irradiation to induce more fission-tracks as a proxy for uranium abundance in the same area counted for fossil fission-tracks. While providing an elegant analytical solution at the ppm level with high spatial resolution (typically <100μm), this approach involves sample turnaround times of mostly several months. Laser-ablation ICP-MS techniques are now able to provide rapid uranium analyses with similar spatial resolution to the older method (Hasebe *et al.*, 2004). This approach greatly improves sample throughput, but has the disadvantage that the target grain and its fossil fission-tracks are destroyed. A combination of automated fission-track counting and laser ablation ICP-MS analysis, however, should prove particulalry advantageous.

Implementation of our automated fission-track counting system requires a microscope with both transmited and reflected light optics, a motorised stage and digital microscope camera, all under computer control. The software system consists of an image acquisition module that automatically acquires a series of reflected and transmitted light images at each area selected for counting. These are archived and a separate automated counting and review module is then used offline to analyse the data. The archived images constitute a digital replica of the mineral grains which are then analysed by laser ablation ICP-MS using the stage coordinates to control positioning. The system has so far been applied successfully to fission track dating of accessory apatite and monazite.

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Water column structure of the Eocene Arctic Ocean from Nd-Sr isotope proxies in fossil fish debris

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Nd-Sr isotopic compositions of Eocene fish debris (teeth, bones, scales) and reduced organic coatings reveal details of Arctic Ocean Basin water column structure at Lomonosov Ridge. Nd in marine fossil fish debris is acquired post-mortem at the sediment-water interface, recording bottom water composition; Sr is metabolized by fish (in this case a variety of smelt) living in equilibrium with their surroundings, recording the $^{87}Sr/^{86}Sr$ of the photic zone. Samples from IODP Expedition 302 all record isotopic values consistent with a brackish-to-fresh water surface environment ($^{87}Sr/^{86}Sr$ = ~0.7079-0.7087) that was poorly mixed with Eocene global seawater (~0.7077-0.7078). Leaching experiments show reduced organic coatings to be consistently more radiogenic (~0.7090-0.7094) than cleaned ichthyolith phosphate. Ichthyolith Sr isotopic variations likely reflect changes in localized river input as a function of shifts in the Arctic hydrologic cycle. We suggest that $^{87}Sr/^{86}Sr$ might be used as a proxy for salinity of surface waters. Model mixing calculations indicate salinities of ~5 to ~20 per mil, close to but lower than estimates based on O isotopes. Significant salinity drops (*i.e.*, 55 Ma PETM and 48.5 Ma Azolla event) do not show large excursions in $^{87}Sr/^{86}Sr$. Epsilon Nd in cleaned ichthyoliths (-5.7 to -7.8) overlaps Neogene Arctic Intermediate Water (B. Haley, pers. comm.), distinct from modern AIW (-10.5) and North Atlantic Deep Water. Eocene ichthyolith Nd may record some deep-water exchange with Pacific/Tethyan water masses, but inputs from local sources are also permissible. The Sr-Nd isotopic record is consistent with highly restricted basin-wide circulation in the Eocene, indicative of a poorly mixed ocean and highly stratified water column with anoxic bottom waters. A stable, "fresh" water upper layer was likely a pervasive feature of the Eocene Arctic Ocean, recording enhanced continental runoff during an unprecedented warm interval lasting from the 55 Ma PETM to the first appearance of ice rafted debris at ~45 Ma.

Trace element zonation of plagioclase from the Kunene Intrusive Complex (NW Namibia)

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The Mesoproterozoic Kunene Intrusive Complex (NW Namibia) consists of two main anorthosite bodies. A pale coloured so-called *white anorthosite* is intruded by the *dark anorthosite* which comprises leucogabbronorites, anorthosites and leucotroctolites.

Anhedral cumulus plagioclase of the *white anorthosite* is often turbid due to post-emplacement alteration. The An contents range from 40 to 50 mol.%. Individual grains either display a constant composition or minor An variations (±5 mol.%) which in some grains appear oscillatory with wavelengths of up to 1000 μm.

Anhedral to subhedral tabular coarse cumulus plagioclase of the *dark anorthosite* is optically clear and contains dust like Fe-Ti oxide inclusions. The An contents range between 43-75 mol.%. Some plagioclase phenocrysts display oscillatory zoning with wavelengths of up to 1500 μm and differences in the An-content of up to 8 mol.%, whereas others are characterized by a homogeneous composition.

Oscillatory zoning patterns of plagioclase from both anorthosite units are interpreted to be igneous in origin, reflecting movements of the crystals in the magma reservoir. Plagioclase phenocrysts that display a nearly constant composition, on the other hand, are suggested to be affected by a post-magmatic reequilibration.

Since plagioclase is the main mineral present in anorthosites, major and trace element zoning patterns can provide important information about processes like cumulate formation, ascent of magma, and possibly also post-emplacement alteration. LA-ICP-MS analyses on profiles across plagioclase phenocrysts are in progress to examine the behaviour of the trace elements during the different stages of anorthosite formation.

Exhumation histories of high-pressure rocks: New insights from Rb-Sr geochronology

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High-pressure (HP) rocks can be considered as 'flight recorders', potentially recording their individual P-T-time-deformation path through evolving orogens. Reading the flight recorder requires both deciphering of the geochronological information, and correlating it with data on pressure, temperature and tectonometamorphic processes. Isotopic signatures of minerals, like the Rb-Sr system of white mica, has long been considered as particularly sensitive to temperature. This often prompted direct translation of sets of mineral ages into cooling histories, with inference of exhumation paths from thermal histories. However, this approach is problematic because microscale spatial correlations of isotopic ages with mineral growth zonation and recrystallization fronts (Vance *et al*. 2003) indicate that factors like availability of fluids, mineral recrystallization, and the modal rock composition similarly play vital roles in determining whether an isotopic system remains closed.

As an alternative approach, assemblages which remained closed for intermineral isotope exchange can be used to generate Rb-Sr 'event ages' for specific metamorphic processes. It is shown that the Rb-Sr system of white mica in eclogite may persist unchanged even through very high temperatures (>650°C). Key requirements for this high thermal stability are a) absence of free aqueous fluids after crystallization, evidenced from absence of fluid-mediated retrogression reactions, and b) modally controlled closed system behaviour, i.e., presence of white mica in an assemblage solely of phases like garnet and omphacite which do not allow for significant diffusional Sr isotope exchange even at the highest temperatures reached. A valid Rb-Sr multimineral isochron comprising all phases of an eclogite assemblage can be interpreted as dating eclogitization (cf. Glodny *et al.* 2005), and directly linked to PT data from the same sample to constrain eclogitization conditions.

The same concept applies to assemblages formed later in a HP rocks' history. Veins, precipitated from fluids during exhumation, may be used to determine age and PT conditions of amphibolite- or greenschist facies overprints. Different event ages combine to an exhumation history, established beyond the pitfalls of closure temperature theory. Using examples from the Tauern Window (Austria) and the Bergen Arcs (Norway), the potential of this approach to precisely constrain contrasting exhumation histories is demonstrated.

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Topographic threshold values for the interpretation of low-temperature thermochronology

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Low-tempertature thermochronology provides the opportunity to quantify surface processes over geological time scales. Deducing exhumation rates is crucially depending on assumptions about the shape of isotherms. Here we present apatite fission track (AFT) data sampled along a horizontal structural level, allowing to reconstruct the critical paleo-isotherm. Samples have been collected along the 16 km long Gotthard road tunnel in central Switzerland and the corresponding surface line. The study was accompanied by 3D numerical thermal modelling, which was carried out incorporating thermally relevant parameters and mechanisms, e.g. topography, geology, thermal conductivities, heat production. Modelling predict a net topography-induced perturbation of the 110°C isotherm of around 250 m, whereas spatial variable heat production rates are capable to produce a perturbation of 550 m. Modelling shows that the effect on near surface isotherms due to spatial variations of thermal conductivities are small. Measured AFT-ages broadly range around 6 Ma along the tunnel. No correlation of ages with overburden and topography can be seen, demonstrating that topography induced perturbation of isotherms under given boundary conditions (topographic wavelength: 12 km, relief 1.7 km, exhumation rate: 0.45 mm/y) and physical parameters of the Gotthard transect can be neglected for the interpretation of AFT-ages. Thus in areas characterised by similar topographies, apparent exhumation rates deduced from age elevation relationship (AER) need no corrections for topography-induced perturbation of isotherms.

Inferences for the style of subduction in the Carpathian-Pannonian region based on boron signatures

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Miocene calc-alkaline (CA) volcanic suites – more or less parallel with the Carpathian Mt. range – suggest a southwest-westward subduction process. Indeed, composition of the CA volcanic rocks shows typical subduction-related features, such as elevated LILE and relatively depleted HFSE. Boron, a fluid-mobile, incompatible trace element can be effectively used to monitor the subduction influence along the arc. In general, the boron concentration of the CA volcanic rocks of the region is typical of subduction-related magmas; however, it shows both significant spatial and temporal variations.

In the western segment of the arc, we cannot see a clear variation in the B content, nor in the B/Nb ratio towards the back-arc region, such as was found in other arcs (e.g., Japan and Kurile, Kamchatka). However, a gradual temporal decrease of these values can be observed. These features can be explained by the strong connection of the CA volcanism in this segment to the lithospheric extension of the Pannonian Basin, more than to the southward dipping subduction.

In the eastern segment of the region, the volcanic arc is narrower. Here, volcanism is getting to be younger towards the southeast. The boron content is increasing to the south along the arc; however, a sharp decrease can be observed at South Harghita. This is consistent with the change in the overall composition of the volcanic rocks and the position of the Trotus fault, which divides two main lithospheric domains.

In the northeastern part of the arc, a kind of transition is observed. At first sight, no correlation can be recognized between the B content and the spatial and temporal distribution of the volcanics. But separately, in the more basic and in the more silica rich rocks, we observe a B content decrease towards SSE. The present volcanologycal information is too incomplete to understand this. It may indicate the influence of the subduction-related fluids originating from a previously existing subducting slab under the Tokaj region.

Electrodynamic disaggreagation of geologic material

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A series of tests were run on a selFrag Lab electrodynamic disaggregation machine produced by selFrag AG, Langenthal, Switzerland. The operation principle is an electrical discharge passing trough a non-conductive material (e.g., rock) immersed in a dielectric liquid. The electrical pulses are of very short duration (<500 ns). In this case, the solid material becomes the better conductor, and hence the electrical "discharge channel" will pass through the solid material. High amounts of energy are deposited along this discharge channel leading to local temperature of up to 10000 ºK and pressures of up to 10^{10} Pa (Rudashevsky *et al*., 1995, Andres and Timoshkin, 1997), thus conditions reached by using conventional explosives.

The tests using different geologic material immersed in deionised water showed that electrical discharges as low as 80 kV and a few hundred pulses at a frequency of 1- 5Hz are commonly sufficient to disintegrate rocks or other mineral aggregates. Accessory minerals separated at voltages of 80 – 100 kV retain their original shape (e.g. zircon, apatite, magnetite); the minerals may break under increased energy input. Sieves replacing the reactor vessel bottom allow small enough material to be removed during operation, and hence to prevent further grain size reduction. Major rock constituents generally disaggregate mainly along internal impurities or fissures, leading to a grain size reduction. However, the minerals contain fewer inclusions. Rare artefacts of the method are formation of melt films, and contamination by very small particles derived from the electrode material. The amount of contamination from the electrode material is much lower than by using conventional crushing methods. A closed disposable microcontainer allows to disaggregate sub-gram samples for microanalysis minimizing loss. Preliminary result did not show negative effects on isotopic systems.

Major advantages in comparison with conventional methods (jaw crusher, vibration disk mill, ball mill) lie in the reduction of fines, the omission of dust, the production of inclusion-free and/or isometrically shaped products, and the reduction of cross contamination.

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From phosphors to ceramic magnets stability, crystal chemistry and applications of hexa-alumintates and -ferrites

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The groups of hexa-aluminates and -ferrites exhibit a wide range of applications. From lamp phosphors in the case of Ba-aluminates (Eu & Mn doped – green, Eu doped – blue luminescence) to ceramic magnets such as Sr-ferrites doped with Co and La a wide range of daily applications can be presented.

In the group of hexa-phases compounds exhibiting magnetoplumbite- and beta-alumina structures are stable. A wide crystal chemical variety gives rise to numerous properties with large potential for chemical fine tuning.

Phase relations and crystal chemical aspects like solid solution series in the multicompound systems $CaO/SrO/BaO/EuO/La_2O_3 - Al_2O_3/Fe_2O_3 - MgO/CoO$ are presented and discussed. The crystal structures present can be explained as mixed layer structures. Starting from the spinel structural type modifications consisting of rock salt-units and perovskite-units build up the different hexa-phases.

Furthermore shaping aspects like ceramic foams consisting of Ca-aluminates aiming towards catalytic applications will be presented.

Indications for pedogenic formation of perylene in terrestrial soil: First results from stable carbon isotope ratios

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Concentrations and isotope compositions of polycyclic aromatic hydrocarbons (PAHs) were determined in natural soils of Southern Germany. Surprisingly, perylene concentrations increased with soil depth when compared to the other PAH compounds present, but only in specific profiles. Its low solubility made vertical transport by seepage water unlikely. We therefore stipulate atmospheric deposition of combustion-derived perylene in the top-soil and *in-situ* generation in the sub-soil of these selected profiles. This could have been caused by microbial activities or other catalytic processes yet unknown. In order to distinguish between pyrogenic and natural generation we compared compound-specific $^{13}C/^{12}C$ ratios ($\delta^{13}C$) between perylene and other PAHs in samples from the top-soil and from the sub-soil. Despite high amounts of co-extracted non-target compounds and low perylene concentrations relative to other PAHs (benzo(e)pyrene and benzo(a)pyrene) successful clean-up of the extracts led to determination of a unique $\delta^{13}C$ value for perylene in the upper horizon. The $\delta^{13}C$ value of perylene in the sub-soil was 3.4 permille more negative than for top-soil perylene, and 5.2 permille more negative than other equal-mass PAHs (with m/z of 252) in the top-soil. Future work will include isotopic characterization of atmospheric input and in situ synthesis of PAHs.

Modelling continental weathering: from the lab to the field

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CO_2 consumption through continental silicate weathering at the watershed scale has been generally described as a parametric function of mean annual continental runoff and temperature, based on river chemistry . These mathematical expressions have been succesfully used in numerical modelling of the evolution of the past geochemical cycles and climate. They have the advantage of integrating numerous processes (hydrologic, biospheric, and kinetic) and to rely directly upon field constraints, but they leave us without any access to the intimate processes of chemical weathering, and do not allow a hierarchization of its controlling factors. Here we present sensitivity tests performed with the WITCH numerical model which describes weathering in soil profiles through vertical multiple box modelling based on a rigorous description of mineral-water interactions. This model is coupled to a vegetation productivity model, and we explore the response of continental vegetation on weathering. We also test the impact of using laboratory-based kinetic weathering rates to estimate the main cation fluxes exported from the soil profile. We show that such method does not lead to any large overestimation of the CO_2 consumption, if the chemical affinity of reactions, and secondary minerals precipitation rates in soils are accurately accounted for. Sensitivity of the kinetic model WITCH to drainage and annual mean temperature is compared to the sensitivity expected from field parametric laws. Particularly, we show that parametric laws underestimate by one to two order of magnitude the weathering rates at low runoff (below 100 mm/yr), while the agreement is good at higher runoff. Although the specific contribution of the low runoff areas to the CO_2 consumption is low, they are typical of the weathering regime of 44 % of the total continental surface.

Interaction of calcite with Cr(III) and evidence for direct inorganic formation of vaterite

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The interaction of freshly cleaved $\{10\bar{1}4\}$ calcite surfaces with 100 mg/L (~2 mmol/L) Cr^{III}_{aq} solutions was investigated at room temperature under atmospheric conditions using *in-situ* AFM for a time-period of up to 20 min. It was observed that the initial typical nanoscale dissolution features (rhombohedral etch pits) are successively filled with matter up until the final overgrowth of spheroidal-like particle aggregates. *Ex-situ* experiments with variable time exposures (1 min, 20 min and 1 month) were also carried out in order to study the surface of the interacted calcite crystals using a combination of techniques. A detailed SEM-EDS, XRD and FTIR study of the experimental products revealed that the surface precipitates consist of amorphous Cr^{III} hydroxide/oxyhydroxide phases. EPMA (WDS) elemental maps on polished-thin sections of teeth-like material removed from the solid interface after long-term interaction (1 month) indicated the formation of a peculiar carbonate phase containing both Ca and Cr in variable concentrations. It should be noted that distinct Ca carbonate (or even hydroxycarbonate) solid phases containing Cr(III) are rather unknown in nature, except maybe the case of a meteorite. Preliminary computational investigations showed a difficulty of Cr^{3+} ions to be hosted in the calcite surface structure.

On the other hand, detailed XPS and Laser μ-Raman studies of $\{10\bar{1}4\}$ calcite surfaces interacted for 20 min with Cr^{III}_{aq} solutions indicated the presence of vaterite. In this case, the thickness of the Cr(III)-modified carbonate surface was investigated using accelerator-based techniques, namely ^{12}C-RBS. The formation of vaterite on the surface of calcite, and in general the direct inorganic formation of vaterite in the presence of Cr^{III}_{aq}, was also confirmed by means of macroscopic experiments aiming at crystal growth of $CaCO_3$ into appropriate glass tubes filled with Cr(III)-doped hydrogel.

Extreme Hf isotope signals from basement weathering and its influence on the seawater Hf-Nd isotope array

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Differential weathering of Lu and Hf host minerals in rocks leads to Hf isotope composition of river water with a more radiogenic composition than the bulk rock that they drain [1]. In contrast, the Nd isotope composition of river water is very similar to that of bulk rock due to congruent weathering of Sm and Nd from their shared mineral hosts. We measured Hf and Nd isotope ratios in seawater and from the Hudson River in NY. The Hf isotopic composition of the upper Hudson draining Grenville-aged metamorphic rocks is extreme, with ε_{Hf} values of +24 to +128. Associated marble and amphibolite bedrock have normal crustal ε_{Hf} values (0 to −11), whereas apatite and garnet from these rocks have ε_{Hf} values as high as +2250 and +103 [2,3]. In contrast, Nd compositions of the upper Hudson are similar to bulk rocks (ε_{Nd} = -8). After the Mohawk River, which drains Ordovician-Devonian limestone and shale, joins the main stem of the Hudson, river water ε_{Hf} and ε_{Nd} decrease to +6 and -10. On the New Jersey Bight, ε_{Hf} and ε_{Nd} are +3 and -8.

The Hf and Nd isotope composition of filtered seawater in the Atlantic overlap data for ferromanganese nodule crusts. Vertical profiles exhibit almost negligible ε_{Hf} gradients suggesting rapid vertical, but little lateral, transport. Surface water ε_{Hf} is less radiogenic close to the Saharan dust plume suggesting an eolian source of Hf with a signal that is not fractionated through weathering processes.

We suggest that the radiogenic Hf character of the seawater Hf-Nd array is due to the preferential weathering of high Lu/Hf phases in basement rocks such as apatite. When this source rock is old evolved crust, dissolution of these high Lu/Hf phases contributes a very radiogenic Hf isotope composition, as evidenced by the upper Hudson river water samples. This differential chemical weathering will be prominent at times when there are no glaciers, and particularly prominent when glacial action has exposed fresh surfaces containing less resistant minerals to weathering [4].

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The source and fate of silica in mineralized porphyries revealed by SEM-CL textures of quartz

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Economic mineralization in porphyry systems (e.g., Cu-Mo-Au) is traditionally attributed to precipitation from metal-enriched hydrothermal fluids that derive at the closure of crystallization of andesite-dacite magmas. Different forms of silica (mainly quartz) are dominant in such systems, and thus controversial in terms of silica solubility in aqueous solutions, amounts of magmatic H_2O, and rates of the fluid flow. The compositions of mineralizing fluids, as argued by the fluid inclusion research, are dominantly chloridic and often halite-saturated, and thus the absence of chloride minerals precipitated with ores remains enigmatic.

We studied shapes and textures (by optical, cathodoluminescence-CL and backscattered electron-BSE microscopy) of quartz grains, and distribution of quartz-hosted fluid inclusions in different porphyries (Batu Hijao, Indonesia; Climax, USA; Panguna, PNG; Dinkidi, Philippines; Rio Blanco, Chile). Silica (analyzed as SiO_2) is present throughout the groundmass as interconnected network of shapeless blebs and individual quartz grains (0.2-2 mm). Most quartz grains are round or even spherical in shape (so-called "quartz eyes"), and have distinct zoning or layering in CL. The number of layers/ bands varies from a few to several tens, and have shapes from nebulous to ellipsoidal to perfect crystallographic. Egg-like and crystallographic shapes of layers are found interspersed within a single grain. The bands are randomly intersected by healed fractures (usually dark in CL), which are always decorated by aqueous ± salts fluid inclusions. The fractures often cause rupture, displacement and inflection of some bands towards the core of grains. Where large fractures intersect the grain surface the outmost bands are spit and curved towards the fracture. The splits are conical in shape and filled with the groundmass. Although such splits look like typical embayments, the curved banding around them is inconsistent with quartz dissolution. The fractures in split grains often border several domains with individual solidification history. In many cases crystallization from internal fracture or from the outermost boundary of the quartz grain can be implied from the observed banding.

The textures of quartz grains are inconsistent with their origin as phenocrysts. We envisage in-situ segregation of residual SiO_2- and H_2O rich liquid (e.g. silica-gel) into blebs and globules after magma emplacement. The solidification of globules was unlike crystallization, as they were developing coeval banding and fractures (possibly as a result of compaction). They possibly remained in a plastic state even at low temperatures, when healing of fractures and trapping of fluid inclusions occurred.

Cosmogenic nuclide intercalibration and erosion rate study on fault scarps of the Bishop Tuff, CA, USA

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The Bishop Tuff in eastern California is a welded ignimbrite deposit that erupted 760 ± 2ka ago from the Long Valley Caldera, as dated with $^{40}Ar/^{39}Ar$ on sanidines [1]. Surface samples from the Bishop Tuff were collected for comparing the production rates of cosmogenic nuclides (^3He, ^{21}Ne, ^{10}Be, ^{26}Al) in various minerals available in the sampled ignimbrite unit, like quartz, pyroxene, magnetite and sanidine. Although the Bishop Tuff has experienced erosion and absolute calibration is thus not possible, still production rate ratios can be assessed. So far, 20 samples have been analyzed for the ^{21}Ne concentration in quartz. For one of those samples, ^3He and ^{21}Ne have been determined in coexisting clino- and orthopyroxene. The concentrations of cosmogenic ^3He are difficult to assess due to possible contributions of both magmatic and nucleogenic ^3He. However, the ratios of cosmogenic $^{21}Ne(cpx)/^{21}Ne(qz)$ and $^{21}Ne(opx)/^{21}Ne(qz)$ are ~1.23 and ~1.45 respectively. In comparison, using the elemental production rates of Kober *et al.* (2005) [2], would imply ratios of ^{21}Ne (px)/$^{21}Ne(qz)$ 1.38 (cpx) and 1.50 (opx) for the chemical composition of these analysed pyroxenes. In the near future we would also like to determine the production rate ratios $^{21}Ne/^{10}Be$ and $^{21}Ne/^{26}Al$ in the same quartz samples.

In addition to the production rate nuclide intercalibration, we performed an erosion rate study at the Bishop Tuff. We sampled the footwalls of 3 normal fault scarps, extending from the fault center to the tapering end, that run N-S through the SW of the Bishop Tuff due to tectonic extension of the area. 18 preliminary exposure ages – calculated from ^{21}Ne concentrations in quartz – range from 260 to 505 ka, i.e. ~35 – 70 percent lower than the eruption age of the Bishop Tuff. The discrepancy shows that about 1.0 to 1.8 m of material has been removed since the eruption. The ^{21}Ne ages vary rather systematically with the oldest ages mostly at the tapering ends of the scarps and the youngest ages at the fault centers where the vertical displacement is maximal. As the faults are active and they propagate [3] our data indicates that the process of erosion is more pronounced on the fault centers compared to the lower fault tips. In general, ages from bedrock samples (n = 14) show more variation than desert pavement samples (n = 4).

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Crystal orientation selection during growth of brachiopod shell calcite

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The progresses in the technique of electron backscatter diffraction (EBSD) in combination with SEM provides an ideal set of imaging and diffraction methods to reveal the architecture of calcitic brachiopod shells. Usually calcitic brachiopods show a two-layered shell with a hard nanocrystalline primary layer and a fibrous secondary layer where the fibers are single crystals with the morphological fiber axis perpendicular to the crystallographic c-axis.

The investigated species, *Kakanuiella chathamensis* and *Liothyrella neozelanica* differ from this assembly: the former one is built entirely of hard nano- to microcrystalline calcite whereas the latter one shows a usuall primary layer, but a secondary layer which is prismatic and a fibrous tertiary layer.

Our observations on the interface between the primary and the secondary layer in *L. neozelanica* suggest a mechanism how the unusual crystallographic texture may arise.

Even though *Kakanuiella chathamensis* consists only of primary layer material we observe some textural features and a pattern in the distribution of hardness within the shell.

Figure 1: EBSD-Map of the three layered shell of *L. neozelanica* (black bar down left: 500 μm).

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Earth's core formation aided by flow channelling induced by Rayleigh-Taylor instabilities

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The core formation mechanism remains poorly known. Geochemical constraints by Hf/W systematics indicate a fast process which was largely completed within 33 Ma for the Earth. An unstable gravitational configuration of a dense molten metallic layer overlying a cold chondritic protocore is predicted by most studies, which leads to the formation of a Rayleigh-Taylor instability. We propose the application of Stevenson's (1989) stress-induced melt channelling mechanism in the region surrounding an incipient iron diapir. We therefore perform numerical experiments solving the two-phase, two composition flow equations within a 2D rectangular box with symmetrical boundary conditions. We apply the Compaction Boussinesq Approximation (CBA) and include a depth-dependent gravity. For simplicity we use a constant viscosity for the solid phase and melt-fraction dependent rheology for the partially molten region around the diapir. A systematic investigation of the physical conditions under which the melt channels can form in comparison with the time scale of core formation and whether they are applicable to the early Earth is in progress. As a result, for sufficiently small melt retention numbers iron-melt focussing channels develop within a region of approximately twice the diapir's size. This could lead to effective draining of the surrounding region and might initiate cascading daughter diapirs or the formation of dykes. The mechanism could effectively enhance melt accumulation in the protocore and accelerate the process of core formation.

Tracing oceanic sulphate with phosphorite geochemistry

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Sedimentary phosphorites contain francolite (carbonate fluorapatite) as the major mineral phase. Francolite is thought to incorporate SO_4^{2-} in proportion to its concentration in ambient pore fluids (Jarvis *et al.*, 1994) and thus could be a potential indicator of past seawater sulphate concentrations. This is attempted by relating SO_4/P_2O_5 ratios of recent and ancient phosphorite rocks to ocean sulphate levels.

Phosphorite can form under diverse redox conditions, which can lead to variations in incorporated SO_4^{2-}. By comparing francolite-bound sulphate $\delta^{34}S$ and $\delta^{18}O$ and carbonate $\delta^{13}C$, the impact of sulphate reduction and sulphide reoxidation on sulphate concentrations can be better constrained. Weathering is also considered to lead to the loss of SO_4^{2-} in francolite, and this can be partially evaluated by CO_2 concentrations in francolite. However, our study suggests that sulphate is only lost from associated organics and pyrite during weathering.

The sulphate concentration and $\delta^{34}S$ of phosphorites do not correlate with Ce-anomaly, which is a redox-dependent parameter. The decoupling of REE from SO_4^{2-} and $\delta^{34}S$ may result from the different timings and mechanisms of incorporation of REE and sulphate into the francolite lattice. Therefore, REE do not provide reliable constraints on the degree of preservation of francolite sulphur systematics.

Francolite SO_4^{2-} is found to be lower than previously reported in Miocene phosphorites. This could relate to the removal of all non-francolite S during sample preparation in our study. SO_4^{2-} levels in Neoproterozoic and Cambrian francolites are also low. Uppermost SO_4^{2-}/P_2O_5 ratios from the best preserved samples (from the Miocene, Cambrian and Ediacaran) in our study can be used to constrain minimum SO_4^{2-} concentrations in the ocean.

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Bistability of atmospheric oxygen and the Great Oxidation

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Earth history has been characterized by a series of major transitions separated by long periods of relative stability. The largest chemical transition was the 'Great Oxidation', approximately 2.4 billion years ago, when atmospheric oxygen concentrations rose from less than 10^{-5} of the present atmospheric level (PAL) to more than 0.01 PAL, and possibly to more than 0.1 PAL. This transition took place long after oxygenic photosynthesis is thought to have evolved, but the causes of this delay and of the Great Oxidation itself have been unclear. We show that the origin of oxygenic photosynthesis gave rise to two simultaneously stable steady states for atmospheric oxygen. The existence of a low oxygen (less than 10^{-5} PAL) steady state explains how a reducing atmosphere could persist for at least 300 million years after the onset of oxygenic photosynthesis. The Great Oxidation can be understood as a switch to the high-oxygen (more than 5×10^{-3} PAL) steady state. The bistability arises because ultraviolet shielding of the troposphere by ozone becomes effective once oxygen levels exceed 10^{-5} PAL, causing a nonlinear increase in the lifetime of atmospheric oxygen (Goldblatt *et al.* 2006). The long term redox forcing of the surface system was probably a decrease in reductant input due to a progressive oxidation of the crust (Claire *et al.* 2006). Once the system was in a bistable regime, the Great Oxidation could have been triggered by a perturbation to the carbon cycle too small to leave a carbon isotope signal. Our results indicate that the existence of oxygenic photosynthesis is not a sufficient condition for either an oxygen-rich atmosphere or the presence of an ozone layer, which has implications for detecting life on other planets by remote sensing and for the evolution of multicellular life.

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A coordinated continental and regional soil geochemical survey of North America

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The U.S. Geological Survey and collaborating partners in Canada and Mexico, have initiated a project that will produce a soil geochemical survey of North America. Pilot phase sampling and analyses have been completed along two continental transects, one of which extends from the west to east coasts of the United States along the 38th parallel. The data for a number of elements in this east-west transect reveal geochemical patterns that correlate with bedrock and glacial deposit composition.

One example of soil-bedrock correlation is elevated Cr concentrations in some California soils, which contain 2000-8000 ppm Cr compared to a median of 27 ppm for all samples across the east-west transect. The origin of this Cr anomaly is revealed by a more detailed regional-scale pilot study north of the San Francisco Bay extending from the Pacific Ocean to the California-Nevada border. This regional study incorporates geochemical data from nearly 2000 soil samples. Cr and Ni in these samples display patterns reflecting the underlying geology.

Elevated concentrations of soil Cr (2000-8000 ppm) and Ni (1000-5000 ppm) overlie serpentinite rocks in the foothills of the Sierra Nevada Mountains and in the Coast Ranges west of the Sacramento Valley. Chromium in these serpentinite-derived soil samples is predominantly in a refractory form, as chromite ($FeCr_2O_4$). Soils with Tertiary volcanic and granitic parent material located at higher elevation in the Sierra Nevada Mountains, as well as alluvial soil in the eastern Sacramento Valley, have much lower Cr and Ni concentrations relative to serpentinite soil (less than 100 and 50 ppm, respectively). Surprisingly, soil with elevated Cr and Ni content (150-400 ppm and 60-300, respectively) occurs in Sacramento Valley soil west of the Sacramento River. Chromium in this western valley geographic setting is in a less refractory form than that in soil overlying serpentinite, is more easily mobilized from soil into groundwater, and spatially correlates with the elevated groundwater Cr levels.

The geochemical studies at national and regional scales complement each other. The former targets areas of interest and the latter provides more detailed process insights.

Tracking microbial life in the marine subsurface

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Evidence has grown that deeply buried marine sediments are habitats to living communities of microorganisms, even under scarcity of nutrients and terminal electron acceptors and apparently hostile environmental conditions. The contribution of such communities to element cycling remains elusive, but direct microbiological assays are difficult to conduct due to extreme in situ conditions. We suggest to make use of anorganic, cell-independent proxies to bypass this hassle and propose the application of oxygen stable isotopes of dissolved inorganic phosphate (DIP) in marine pore waters.

The $^{18}O/^{16}O$ ratio of pore water DIP is significantly affected by active microbial phosphate (PO_4) metabolism. The exchange of oxygen atoms between water and phosphate is enhanced by extra- and intrazellular hydrolase enzymes in living cell PO_4 uptake and processing, and can be distinguished from abiotic fractionations during sediment diagenesis (Blake $et\ al.$ 2005). Therefore we consider the $d^{18}O$ of pore water DIP a fairly robust and feasible parameter for the identification and profiling of microbial activity in deep sediment cores.

We here present a modified microextraction technique for marine pore water PO_4. DIP is concentrated by magnesium induced coprecipitation, separated from interferring anions by a preparative ion chromatography using anion exchange resin, and subsequently precipitated as silver phosphate (Ag_3PO_4, Colman 2002). Ag_3PO_4 is finally combusted in an elemental analyzer, and transferred online via continuous flow to an isotope ratio mass spectrometer. The amount of DIP required for the precipitation of crystal Ag_3PO_4 can thereby be reduced to less than 1mg, making an analysis of pore water samples which are limited in sample volume and DIP content possible. On research cruise MSM04-4a with German vessel Maria S. Merian we recovered four sediment cores up to 42m below sea floor offshore Morocco using a remotely operated seafloor drill rig, and took pore water samples with an average depth resolution of 0.5m for the application of the novel technique described above.

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Experimental CO$_2$ and water interactions with Permian coals of Queensland, Australia

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A key issue for geological sequestration of CO_2 is the effect of geochemical reactions between multi-phase fluids and the host strata. We report here the results of batch experiments conducted under simulated in situ conditions (38°C and 90 bar for 60 hrs) to evaluate the chemical and physical changes caused by CO_2 injection into deep coal seams. Experiments were conducted in a purpose built reactor on coal blocks (15 mm to a side) and powders (180-220 μm) using supercritical CO_2 and water (SCO_2-H_2O), supercritical CO_2 (SCO_2) and water (H_2O) alone. The Permian coals used in this study were of similar rank but quite different texture. Coal A has a vitrinite reflectance of 0.9% and is a dull, relatively massive coal. Coal B has a vitrinite reflectance of 0.85% and is a bright, well banded coal.

Leachate chemistry indicates significant mobilisation of metals that results from dissolution of sulfide, carbonate and silicate minerals and displacement of cation exchangable metals from coal. CO_2 alone and H_2O alone mobilise less mineral matter than SCO_2-H_2O and have less impact on coal density and porosity. SEM images provide evidence of dissolution of cleat and matrix minerals that continues during a second 60 hour treatment with SCO_2-H_2O. The 15mm cubes behave differently to each other when treated with SCO_2-H_2O. The bright coal cubes show a decrease in helium density, whereas the dull coal cubes show an increase in helium density. This indicates that coal character influences swelling behaviour and the extent of mineral matter mobilisation. The decrease in helium density and increase in surface areas for the bright coal cubes and coal powders suggests that dissolution of mineral matter in the near injection well area may counterbalance reduction in permeability due to swelling as a result of adsorption of CO_2.

Chemical weathering of Taranaki volcanics, North Island, New Zealand

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New Zealand's North Island watersheds in the Taranaki and Manawatu-Wanganui regions have been subject to volcanism since the Miocene. We sampled water and sediments from watersheds that contain both volcanic and sedimentary rocks. Water and sediment samples were collected and analyzed for major, minor and trace elements, in order to quantify the weathering intensities in the watersheds and to establish the relationship between physical and chemical weathering yields in volcanic lithologies.

Results reveal distinct chemical signatures, with waters draining the Taranaki region volcanics significantly enriched in K^+ and depleted in Sr^{2+} compared to those draining the Manawatu-Wanganui region volcanics, which also traverse expanses of sedimentary siltstones and mudstones. These depletions may reflect the relative absence of $CaCO_3$ in the Taranaki region watersheds. In addition, sediment samples from the Taranaki Region show significant enrichment in Ti, Al, Ca, Fe, Mg, Mn, Mg, Ca, and P and depletion in Si and Rb compared to those of the Manawatu-Wanganui region.

Mineral stability diagrams for streamwater samples show that primary feldspar minerals present would weather to kaolinite while clay minerals would likely be present as kaolinite, illite, or Mg-montmorillonite. Normalized sediment values for the Taranaki region exhibited a best fit pattern to average Mt. Egmont andesite values with relative soluble alkali and alkaline earth elements Na, K, Rb, Sr, and Ba and insoluble elements Ti, Al, and Fe, while normalized values for the Manawatu-Wanganui region exhibited a best fit pattern to near shore mud.

From total dissolved solids concentrations and annual volumetric water discharge, chemical weathering yields of 60–238 tons km^{-2} a^{-1} are obtained. These weathering yields fall within the middle to upper range of those previously reported for New Zealand's Southern Alps (93–480 tons km^{-2} a^{-1}) and East Cape (62–400 tons km^{-2} a^{-1}). Calculated silicate weathering yields of 12–33.6 tons km^{-2} a^{-1} and CO_2 consumption of 852–2390×10^3 moles km^{-2} a^{-1} for the rivers draining the Taranaki volcanic region are higher than those previously reported for watersheds hosted in sedimentary and metamorphosed rock terrains on HSIs. CO_2 consumption is found to be within the range which others have reported for the basaltic terrains of the Deccan Traps (580–2450×10^3 moles km^{-2} a^{-1}) and Réunion Island (1300–4400×10^3 moles km^{-2} a^{-1}). Calculated chemical weathering yields demonstrate the importance of taking into account weathering on high-standing oceanic islands, particularly those with volcanic terrains, when considering global geochemical fluxes.

The nature of the mantle source of Archean ferropicrites

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Although ferropicrites have been recognized as an unusually Fe-rich mafic igneous rock for some time, the nature of their mantle source remains unclear. Ferropicrites are most common in Archean terranes and four occurrences from the Superior craton form the basis of this study: the Steep Rock, Lumby Lake, Grassy Portage Bay, and Dayohessarah Lake greenstone belts. Ferropicrites from the first three belts occur as ash to lapilli tuffs, while those from the latter belt occur as coarse-grained intrusive rocks cutting basalts and komatiite flows. These ferropicrites are mafic to ultramafic rocks (15-23 wt% MgO) characterized by low Al_2O_3 (<8 wt%), high FeO* (15-21 wt%), and relatively high TiO_2 contents (1-2 wt%). They have fractionated REE profiles (La/Yb = 8-20; Gd/Yb = 3-4.5) and relatively high contents of HFSE (Nb = 10-18 ppm; Nb/La = 0.8-3.0). In contrast, coexisting komatiites from Dayohessarah have higher Al_2O_3 (9-11wt%) and lower contents of FeO* (~11 wt%), TiO_2 (~0.5 wt%), HFSE, and LREE, despite having similar MgO contents; they also exhibit flat REE profiles (La/Yb = 1-2).

These geochemical differences require that the two magma types have different mantle sources. Peridotite-basalt mixtures that have been proposed as possible ferropicrite mantle sources fail to reproduce ferropicrite Fe contents. A garnet pyroxenite mantle source does not have sufficient Mg to produce liquids with up to 20 wt% MgO, and an olivine-dominated source seems to be required. Melting experiments on model mantle compositions (KLB-1, Mg # = 89.6) suggest that komatiitic liquids like those at Dayohessarah can be produced at 45 kbar, but do not reproduce the Fe contents of ferropicritic liquids under any conditions. Experimental melts of a model Martian mantle composition (Mg # ~80) at 15 kbar have nearly identical Fe contents to our ferropicrites, and melts produced at 50 kbar have Fe contents significantly higher than our ferropicrites. Interpolation of these data shows that the mantle source of our ferropicrites would have a Mg # of ~80 at 15 kbar, which would require large degrees of partial melting, or a Mg # of ~85 at 50 kbar. In the latter scenario, these ferropicritic liquids would be the result of smaller degrees of partial melting, consistent with their fractionated trace element profiles and lower Al contents relative to komatiites, if garnet were not completely consumed during ferropicrite petrogenesis.

Hf isotopes as the key for distinguishing slab melting in arcs: The case of the Mexican Volcanic Belt

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Convergent margins are important as the global setting where crust is recycled into the mantle and new continent is made. Despite major advances in delineating the processes that control arc magma generation, the problem persists of distinguishing slab, mantle wedge, and crustal contributions, along with the question of whether there is significant melting of subducted ocean crust. Especially in thick crust regions, the importance of crustal versus mantle contributions to lavas represents a long-standing fundamental issue in arc magma geochemistry. We show, based on evidence from Hf isotopes, that frontal arc magmas from the Central Mexican Volcanic Belt (CMVB), including the large andesitic stratovolcanoes Popocatepetl and Nevado de Toluca, display negligible crustal contamination, and contain a component derived from melting of regional subducted oceanic crust plus sediments.

Despite thick continental crust, the CMVB erupts near primitive lavas including "high-Nb" alkaline basalts that show negligible trace element "subduction signatures". The "high Nb" basalts define the regional mantle wedge composition in isotope-trace element space, and show well-defined Hf-Nd-Pb-Sr isotope "arrays". In "normal" CMVB lavas with "subduction signatures", a key feature is that they form trends from the "high-Nb" lavas toward even higher Hf isotope ratios, thus their sources are more "depleted mantle-like" than the regional mantle wedge. Of prime importance here is that higher Hf isotopes in these "normal" lavas correlate with low Lu/Hf and Pb isotope ratios.

These negative correlations can be simply modeled as mixtures of the regional mantle wedge, represented by "high-Nb" basalts, with a low degree composite melt of the subducted slab represented by altered Pacific ocean crust plus DSDP Site 487 sediment, located near the trench. Neither altered Pacific crust nor sediment by themselves explain the "normal" CMVB data, but the ocean crust component predominates. Thus, the integrated data allow us to clearly distinguish between mantle and crustal sources and point to substantial subducted slab melt contributions to these lavas.

It is fitting for a symposium that asks what have we learned from Hf isotopes that we don't know already from Nd, that Lu-Hf provides key evidence identifying mantle signatures in a thick crust arc, and for distinguishing the slab melt contribution from other possibilities. These observations are also significant in the context of global arc data.

Relationships between magnetic properties and heavy metals in *Nerium oleander* leaves and soils (Viseu, Central Portugal)

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Magnetic parameters (χ_{Lf}, ARM, IRM_{1T}) and selected heavy metals concentration (Cu, Fe, Mn, Zn, Pb, and Cr) of *Nerium oleander* leaves and topsoils were determined for 24 samples sites in the urban area of Viseu (Central Portugal). The purpose of this study is to relate magnetic properties to heavy metals concentrations and to assess the urban pollution levels. The table bellow presents some statistical information on the results obtained.

Variables (units)	Topsoils			Leaves		
	n	Min-Max	Mean	n	Min-Max	Mean
χ ($10^{-8}m^3kg^{-1}$)	23	44.9-141.9	78.4	27	2.3-193.2	51.6
IRM ($Am^{-1}kg^{-1}$)	23	155.5-878.8	391.9	27	4.7-120.9	31.3
ARM ($Am^{-1}kg^{-1}$)	23	4.5-39.8	12.3			
Fe (mg/kg)	23	17800.0-61400.0	37239.1	27	207.1-1396.5	766.0
Mn (mg/kg)	23	258.0-833.6	455.5	26	37.7-231.6	108.7
Cr (mg/kg)				27	0.3-6.8	3.3
Zn (mg/kg)	23	18.7-499.9	184.4	27	34.2-126.5	67.7
Cu (mg/kg)	23	19.7-164.8	66.3	27	9.4-44.1	23.4
Pb (mg/kg)	23	16.2-149.0	62.7	24	0.2-2.5	1.2

Significant correlations were found between most chemical elements and magnetic parameters determined in leaves. This is confirmed by a factor analysis, where the dominant factor (60% of the total variance) shows only positive contributions including both physical and chemical parameters (Cu, Fe, Mn, Pb, Zn, magnetic susceptibility, and IRM). The second factor (18% of the total variance) shows positive contributions of Fe and Cr and negative of IRM and magnetic susceptibility. Communalities are higher than 0.82, with the exception of Mn (0.44) and Pb (0.65). The same pattern was observed for topsoils. Again, chemical and magnetic parameters are related with significant correlations and a factor analysis shows positive contributions of all of them to the most important factor (49% of the total variance). The second factor (25% of the total variance) shows positive contributions of ARM and Fe and negative contributions of Pb and Zn. Communalities are all higher than 0.55 and most exceed 0.75.

These results indicate that factor 1 in both cases is clearly related to contamination induced by anthropogenic activities and that magnetic parameters of leaves and soils can be used as an indicator of the degree of chemical contamination and pollution levels. Factor 2 is probably related to natural variations of the composition of leaves and topsoils.

Remediation of azo dyes by natural manganese oxides

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In the present work, the degradation of azo dyes (60 mg/L) and aromatic amines (60 mg/L) in the presence of natural Mn oxides was investigated in batch experiments. A 1/10 (w/v) solid/solution ratio was used.

Discussion

Dyes Acid Orange 7 and Acid Yellow 36 were decolourised by the manganese oxide (natural pH of 8-9), indicating that they were either being degraded or adsorbed onto the mineral surface[1]. As no sterilised Mn oxide samples were used, the possibility of the reactions being solely biologically mediated cannot be discounted. Experiments performed in the absence and presence of nutrients also gave different results.

The biological activity of these systems was assessed by using molecular biological techniques such as DNA extraction followed by Polymerase Chain Reaction (PCR) [2]. Results indicate the presence of microorganisms in all samples analysed.

Conclusions

The ability of natural 'waste' Mn oxide compounds to undergo oxidation and reduction reactions makes them suitable to be used as redox mediators (electron shuttles) in the degradation of azo dyes and aromatic amines in natural environments. It is not clear from these experiments whether this process is either a chemically and/or a biologically mediated processes.

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Biogeochemical and mineralogical characteristics of the acid mine drainage system in Aljustrel and S. Domingos mines, Iberian Pyrite Belt

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Aljustrel and S. Domingos are important mines of the Iberian Pyrite Belt, the former currently active and the latter closed since the sixties. Both systems were sampled and analysed. Samples included old and recent mine taillings, stream sediments, surface waters, and biological material (algae). Acid drainage is very similar in both areas but acid waters in Aljustrel have 7 to 8 times higher metal concentrations than in S. Domingos. However, in S. Domingos the system is much more contained.

Aljustrel: Água Forte stream drains the major taillings. This stream receives domestic waste-waters 2 Km away, which act as a neutralizing agent to the acid waters (pH 2). Waste-waters pH is ≈8, and drops to values near 4 upon mixing with the acid waters. In Summer, acid drainage stops but waters down-stream maintain their pH close to 4. The ubiquitous presence of gypsum and jarosite in sediments and crusts provide a source for acidity due to their dissolution. Sediments down-stream have iron-rich surface layers and dark coloured material in the deeper layers (sulphides?). Modelling results show that such pH values may be attained only if precipitation of iron oxides and sulphides occur during mixing of waters. Water samples from sites with abundant iron-oxide sediments present the association *Acidithiobacilus ferrooxidans*, *Leptospirillum ferrooxidans*, *Acidithiobacilus albertensis*, and *Leptospirillum ferriphilum*.

S. Domingos: Has a much more complex secondary mineral assemblage: gypsum, jarosite, schulenbergite, natrojarosite, szomolnokite, and coquimbite. Along the major flow path from the dams and pits, both water chemistry and parameters do not change apreciably.

Algae from both mining areas were centrifuged to extract part of their water content, and their tissues were dissolved. Concentrations of Cu and Zn in the organic material were 3 to 4 times lower than in the liquid extracts, whose concentrations were about half the corresponding concentrations in the flowing waters. Pb, Co, and Cd have only trace concentrations.

H-O isotopes and water content in nominally anhydrous minerals from UHP eclogite in the Dabie orogen

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Fluid activity during subduction-zone metamorphism is an important issue with respect to chemical geodynamics of continental collision. In particular, it has been intriguing where retrograde fluid comes from during exhumation of deeply subducted continental crust. Mineral water concentration and stable isotope analyses are a powerful means to decipher the origin and nature of aqueous fluid in UHP metamorphic minerals. Using a stepwise heating procedure, a number of FTIR analyses demonstrate that only molecule H_2O is removed from garnet from eclogite, without significant loss of structural OH. A TC/EA-MS online method, together with the stepwise heating procedure, is used to determine both H isotope ratios and concentrations of total water and structural hydroxyl in nominally anhydrous minerals from UHP eclogite at Bixiling in the Dabie orogen, China. The results show total H_2O concentrations of 1791 to 2997 ppm in omphacite and 522 to 981 ppm in garnet, and hydroxyl concentrations of 1242 to 2808 ppm H_2O in omphacite and 279 to 747 ppm in garnet. Except for quartz which has a higher concentration of molecule H_2O (189 ppm) than structural hydroxyl (117 ppm), all of the other minerals have much higher concentrations of structural hydroxyl than molecule H_2O. The eclogite has total water δD values of -112 to $-92‰$ for omphacite and -98 to $-94‰$ for garnet; structural hydroxyl δD values of -91 to $-85‰$ for omphacite and -87 to $-72‰$ for garnet. It appears that the total H_2O is depleted in D relative the structural OH in the nominally anhydrous minerals. The nominally anhydrous minerals have similar δD values to each other, but are lower than δD values of -59 to $-58‰$ for muscovite. On the other hand, hydroxyl δD values for the nominally anhydrous minerals are close to hydroxyl δD values for hydrous minerals. Laser fluorination analysis obtained that the eclogite has an $\delta^{18}O$ value of 2.5‰ for zircon, 2.7 to 3.7‰ for garnet and 3.3 to 4.5‰ for omphacite. They are lower than normal mantle zircon $\delta^{18}O$ values. Both O and H isotope equilibrium and disequilibrium occur between coexisting omphacite and garnet, but retrograde metamorphism occurred with internal buffering of stable isotope compositions. Thus both O and H isotope signatures of minerals from the eclogite indicate incorporation of meteoric water into eclogite protolith by high-T hydrothermal alteration and subsequent magmatism. The meteoric signature was preserved in the UHP minerals during the subduction of continental slab, with only limited activity of fluid within the slab. Nevertheless, fluid became available during exhumation due to a decrease in water solubility with pressure decrease. Therefore, exsolution of structural hydroxyl and molecular water from the minerals is the most plausible source for the retrograde fluid.

A fractal concentration-mass method for geochemical anomaly separation in Shizhuyuan tungsten deposit area

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Anomaly separation plays an important role in mineral exploration. A fractal concentration-mass (C-M) method was presented for separating geochemical anomalies from background. The method is derived from Mandelbrot's coastline length-ruler model by replacing the length with mass and ruler with concentration. In log-log plot, the concentration-mass pattern follows the fractal distribution with uni-scale or multi-scale, which was used to discriminate geochemical processes and to separate geochemical anomaly from background.

The C-M method was tested on stream sediment geochemical data in Shizhuyuan tungsten deposit area, Hunan province in China. The stream sediments were sampled using grid method by 31 multiply 31 kilometers with one sample per square kilometer (n=961). Six elements, W, Sn, Pb, Ag, Ni and Ba, were selected to test the C-M method in this area, in which W, Sn, Pb, Ag with mineralization and Ni, Ba without. The results indicated that multi-scale fractal or mixing-dominant geochemical processes was occurred in this area and the anomaly can be separated from background efficiently. Compared with the typical method (anomaly determined by average plus double standard deviation), the anomaly area of W, Sn, Pb, Ag determined by C-M method is evidently smaller (with larger anomaly value) and more coincident with known deposit sites, and the anomaly area of Ni, Ba is distinctly larger (with smaller anomaly value) and more consistent with the Devonian and pre-Cambrian strata area respectively. Therefore, the C-M fractal method is efficiently in separating geochemical anomaly from background with good qualities in aiming at deposit target promptly or in avoiding losing weak anomaly information.

Geochemical features of the basic-ultrabasic rocks of the Udokan-Chiney region (Siberia, Russia)

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The problem and the main goal of the study

Mantle magma's intrusions inside the Southern framework of the Siberian platform reflect the main destruction episodes on the Earth. They are the Paleopangea falling to pieces in the Early proterozoic époque and the tectonic activity in Kz. To understand the magmatic evolution and the associated ore-forming processes in the Udokan-Chiney region it is necessary to study geochemical features of the basic-ultrabasic rocks from numerous massifs located inside this area.

Results

The composition of the rocks (main and trace elements) from different Paleoproterozoic massifs – Chiney, Luktur, Mylove, and Neoproterozoic massifs – Doros, Udokan Great Dyke, so as the Mz and Kz basalts have been studied by XRF and ICP-MS. In this range (from ancient to modern rocks) there is an evolution of its compositions: close to N-MORB – E-MORB – OIB. La/Yb and Th/Ta ratios of the studied massifs change significantly (fig.1) and demonstrate the role of the different sources in their magma generation.
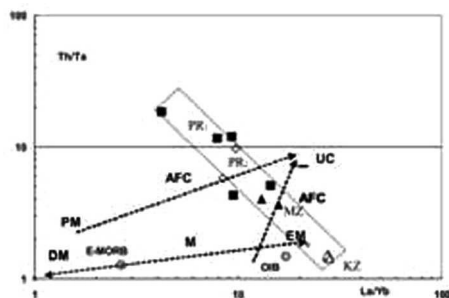

Figure 1: La/Yb vs. Th/Ta diagram for the studied complexes from Udokan-Chiney region.

Nothing paradoxical about Helium concentrations in OIBs

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We show that the He concentration paradox, as well as the full range of noble gas concentrations observed in mid-ocean ridge basalt (MORB) and ocean island basalt (OIB) glasses, can self-consistently be explained by disequilibrium, open-system degassing of the erupting magma. We demonstrate that a higher CO_2 and H_2O content of OIBs, compared to MORBs, leads to more extensive degassing of He in OIB magmas.

Outgassing during melt production at mid-ocean ridges has led to a volatile depleted upper-mantle MORB source with low $^3He/^4He$ ratios. Consequently, $^3He/^4He$ ratios in OIBs, often a factor of 4-6 higher than in MORBs, are conventionally viewed as evidence for an undegassed, primitive mantle source. However, this conventional model provides no viable explanation for why noble gas abundances in OIBs are an order of magnitude lower than in MORBs. This has been called the "He concentration paradox", which has contributed to a long-standing controversy about the structure and dynamics of Earth's mantle.

If, during magma eruption there is insufficient time for all volatiles to diffuse from the melt into gaseous bubbles, the abundance of dissolved volatile species is controlled by both solubility and diffusivity. Because of its relatively high diffusivity, He degassing of OIB and MORB magmas is not significantly limited by diffusion and is predominantly controlled by solubility. On-average higher CO_2 content of OIBs relative to MORBs dilutes He in the exsolved gas phase, thereby lowering partial pressures and decreasing absolute He solubility. This explains why OIB lavas have lower He abundances than MORBs, even though the OIB parental magma is more He rich. On the other hand, degassing of Ne and Ar is limited by diffusion during eruption of both MORB and OIB magmas. When combined with higher He loss in OIBs, this explains the low He/Ne and He/Ar ratios of OIBs relative to MORBs.

The observed noble gas content in OIBs is entirely consistent with degassing of a parental magma derived from a mantle source with a primordial component and total ^3He, ^{22}Ne, and ^{36}Ar abundances of approximately 4×10^{-9}, 1×10^{-9}, and 3×10^{-9} cm^3 STP g^{-1}, respectively. The percentage of primitive mantle component in the OIB source is on average less than 20%, but our present calculations do not constrain the size nor the location of the primitive reservoir. Regardless of whole mantle convection, it appears that part of the Earth's mantle has remained relatively undegassed and primordial in volatile content over Earth's history.

Mud-breccia clasts and sediments as nucleation sites for hydrocarbon-derived ferromanganese nodules in carbonate-mud mounds from the Gulf of Cadiz

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During the Anastasya-01 cruise (TASYO project), extensive nodule fields were discovered and sampled for the first time at water depths ranging from 850 to 1000 m, associated with hydrocarbon-derived carbonate chimneys and crusts in the Guadalquivir Diapiric Ridge area (eastern Central Atlantic) [1]. Nodules show a wide range of sizes and predominantly tabular shapes. They are formed of multiple millimetre-thick layers of Fe and Mn oxides surrounding the nucleus composed of Early-Middle Miocene plastic marls and mud-breccia sediment, which were derived from underlying units by fluid venting. Fe-Mn layers and carbonated cores display the same microtextural features, composed by zoned rhombohedral crystals (authigenic Fe-Mn oxides in layers, and siderite to rhodochrosite in the nuclei) surrounded by detrital grains (silicates) and framboidal associations (fresh pyrite or totally pseudomorphised by goethite). The center of the rhombohedral crystals are enriched in manganese and their exterior edges are iron enriched for both, Fe-Mn oxides and Fe-Mn carbonates. Nodules show a high mean abundance of Fe (38.6%) moderate Mn (6.0%), and low contents of trace metals and REEs compared to the average content of deep-seabed polymetallic nodules [2]. The studied nodules hold in their oxide layers and cores hydrocarbons (n-alkanes), with a first concentration maximum at n–C_{18}, derived from marine bacterial activity, also with presence of aromatic hydrocarbons as phenanthrene, characteristic of mature petroleum. Bacteria-mediated oxidation of hydrocarbons through Mn^{4+} and Fe^{3+} reduction, could be related to the precipitation of Fe-Mn carbonates and sulphides, forming siderite-rhodochrosite concretions bellow the redox boundary within the sediment, that later were transformed into ferromanganese-oxide nodules by exhumation and exposition to the sea bottom oxidising waters.

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A noble gas approach to fluid origin in mesothermal gold deposits, Otago and Alpine Schists, New Zealand

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Mesothermal gold deposits are economically significant on a global scale yet the origins of both the gold and the mineralizing fluids remain poorly understood. The relative contribution and mixing of meteoric, magmatic and metamorphic derived fluids is not well known and may involve complex fluid evolution, mixing and unmixing.

Noble gases are ideal tracers of fluid origin in crustal materials due to their chemical inertness and low abundance. The atmosphere, mantle and crust have unique noble gas isotope fingerprints that are resolvable, as is the relative contribution of these components as the fluid evolves. Magmatic fluids are identifiable by primordial ^{3}He and crustal fluids by radiogenic isotopes, such as ^{4}He and ^{40}Ar. The presence of a diluted dissolved atmospheric signature may indicate the mixing of meteoric and metamorphic fluids and the degree of isotopic or elemental fractionation can identify unmixing processes such as boiling.

We focus on two mesothermal gold systems in New Zealand. These are Mesozoic economic deposits hosted in the Otago Schists and Pliocene-recent gold bearing quartz veins in the Southern Alps (Alpine Schist). The latter study provides a suite of quartz vein samples from a variety of crustal depths to the brittle-ductile transition to investigate meteoric fluid penetration versus metamorphic fluid buoyancy in the Southern Alps. The absence of any igneous bodies simplifies potential fluid sources. Initial results from Southern Alps samples confirm the predicted absence of magmatic fluids, with no resolvable magmatic ^{3}He component. Crustal radiogenic (e.g. ^{4}He and ^{40}Ar) and meteoric water-derived noble gases (e.g. ^{20}Ne and ^{36}Ar) are readily resolved and will enable us to identify fluid source and mixing process.

Slab-mantle interaction and petrogenesis of interplate basalts

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Interplate basalts have been produced from mantle reservoirs which content of protoliths of former oceanic crust. The peculiarity melting of these sources were studied experimentally at temperature range 1250-1400ºC and pressure 1.5-4.0 GPa by using the peridotite ampoule method. In peridotite-basalt-volatile (H_2O or H_2O+CO_2) systems (PBV) as the model such reservoirs high magnesian melts (14-18 % MgO) in equilibrium with Opx+Cpx formed by react slab-derived liquids with mantle peridotite ("reaction" melts). Their volume depend on volume basalt of slab. In the some experiments during partial melting of peridotite formed 3-5 % "filmy" andesitic or more high siliceous (up to 60 % SiO_2) liquids.

Figure 1: Photo of experimental sample in the backscattered electrons. T=1250 C, P=2.5 GPa, 5% H_2O+CO_2
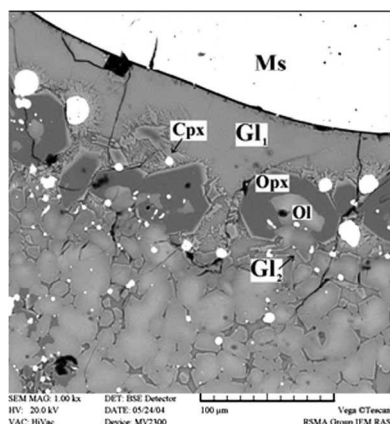
Make allowance of volume slab basalts my proposed, that the slab-mantle sources would be produced more bigger volumes of magnesian basalts at comparatively lover temperatures to compare with normal partial melting of peridotite. All these observations, based on experimental study PBV systems, probably may extent to petrogenesis of interplate basalts.

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Bacterial nanowires: Extracellular electron transfer and mineral transformation

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Dissimilatory metal reducing bacteria use solid phase iron and manganese oxides as electron acceptors and couple this enzymatic reduction to growth. This mode of anaerobic respiration profoundly influences mineralogical transformation in diverse natural environments. But the use of metal oxides as electron acceptors presents challenges to bacteria that must coordinate transfer of electrons from bacteria to the mineral surfaces. Recent results demonstrate that metal reducing bacteria, such as *Geobacter* and *Shewanella* spp., produce electrically conductive appendages called bacterial nanowires under conditions that limit availability of electron acceptor (Reguera *et al.*, 2005; Gorby *et al.*, 2006). A combination of scanning electron microscopy (SEM) and scanning tunneling microscopy (STM) confirmed that wild type *S. oneidensis* MR-1 produced electrically conductive nanowires that connected cells together into an electrically integrated cellular network. Conductivity of *Shewanella* nanowires requires the presence of cytochromes, which were previously shown to enzymatically reduce solid phase Fe(III) and Mn(IV) minerals (e.g. Beliaev *et al.*, 2001). Mutants lacking these electron transport proteins produced appendages resembling nanowires that were not conductive. These mutants did not reduce Fe(III) (hydr)oxides, produce electricity in microbial fuel cells, or form thick biofilms (Gorby *et al.,* 2006).

Nanowires are not exclusive to dissimilatory metal reducing bacteria. Organisms ranging from oxygenic cyanobacteria to thermophilic syntrophic bacteria produce electrically conductive nanowires (Gorby *et al.*, 2006). Structure resembling nanowires are commonly observed in iron oxidizing environments. This presentation will provide our current understanding of the diversity, distribution, and implication of bacteiral nanowires in a variety of microorgansisms.

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Melting and mixing processes in mantle wedges

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Partial melting of mantle and subducting slab material is one of the crucial mechanisms of mass transfer in subduction zones. To study the dynamics of this phenomenon we used 2-D coupled petrological-thermomechanical model with different tectonic setups (i.e. intra-oceanic subduction and active continental margin). To simulate water propagation and magmatic processes we implemented slab dehydration, partial melting and hydration of mantle wedge. We studied mantle wedge processes in various resolutions (form 0.5 million to 10 billion markers) to resolve complexity of theses processes.

Hydrated and partially molten material (plumes) rise through the mantle wedge along trajectories determined by the balance between buoyancy force and mantle flow. Their geometries differ depending on physical properties of mantle and diapir as well the dynamics of the system. Variations in plume development have influence on surface processes like slab retreat and speed of back-arc opening or rotation of fore-arc.

Slab plumes material can be homogenous (only mantle material) or heterogeneous (mantle and slab material). In case of heterogeneous plume during its growth materials mix chaotically resulting in attenuation and duplication of the original layering on scales of 1–1000 m. This process may verify marble cake theory and explain existence of complex peridotitic structures exhumed to the surface.

The use of overbank sediments data for geochemical mapping and contamination assessment: Results from selected floodplains of Serbia

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Introduction

Profiles made from the data of the overbank sediments from the flood plains of Serbia contain the geochemical inscription of the depositional milieu of the preindustrial era. Taking into consideration that they represent wider drainage areas together with the stream sediments, they were used to create regional geochemical map. Contents of the certain chemical elements from the overbank and stream sediments along with anthropogenic influence on the certain localities were represented on the map.

Discussion and results

Geochemical prospecting and mapping were done in accordance with the criteria of the West European Geochemical Surveys (WEGS). The area of the East Serbia drained by the river Timok with its tributaries was selected for investigations. Differences in Pb, Zn, Cu, Au, Sb, As, Cd, Cr, Ni, Co, V and other elements were noted in overbank and stream sediments of the main flow and its tributaries. The contents of certain elements are presented in the table below:

Values (ppm)		Pb	Zn	Cu	Au	Sb
River	OB	12	62	28	0.02	<1
Timok	STR	18	190	38	0.02	<1
Borska	OB	34	60	300	0.04	15
River	STR	80	75	6222	5.54	5
Crni	OB	41	59	84	0.12	2
Timok	STR	50	348	139	0.05	20
Values (ppm)		As	Cd	Cr	V	
River	OB	-	<0.1	91	66	
Timok	STR	-	<0.1	93	190	
Borska	OB	20	1.2	40	10	
River	STR	7	0.8	35	90	
Crni	OB	2	1.5	130	100	
Timok	STR	40	1.5	50	40	

OB= overbank sediments; STR = stream sediments

Conclusion

Obtained results are presented on the geochemical maps of the Eastern Serbia, on the diagrams, tables and geological cross sections. Obvious differences in concentrations of certain elements from overbank and stream sediments reflect anthropogenic influence on the environment.

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Lifetime of the active solar nebula

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The duration of formation of the very early solar system objects, such as the Ca-Al-rich Inclusions (CAIs) and chondrules, that are considered to be products of high temperature nebular processes, effectively defines the lifetime of the active solar nebula. Most of the CAIs host radiogenic isotopic anomalies from in-situ decay of short-lived now extinct nuclides, while a subset of CAIs are devoid of such anomalies but host large magnitude stable isotope anomalies. The latter group appears to have formed in the solar nebula within the first 10^5 years, prior to the injection of freshly synthesized short-lived nuclide into it [1]. The formation of the CAIs hosting radiogenic isotope anomalies spread over a time scale of a few times 10^5 years [2], although recent data suggest that this could be as short as 5×10^4 years [see, e.g., 3]. There is a general consensus at present that formation of chondrules started about a million years after the formation of the CAIs, and the inferred duration of chondrule formation, based on study of ^{26}Al records, varies from less than a million years to three million years [3]. A detail study of chondrules from unequilibrated ordinary chondrites (UOCs) belonging to the L group and representing various petrologic types, show that the major episode of chondrule formation started ~1.5 Ma after CAI formation and lasted <1Ma [4]. The longer duration of formation for UOC chondrules, inferred in earlier studies, appears to be an artifact caused by thermal metamorphism affecting some of the chondrules belonging to low petrologic type. In contrast, data for chondrules from carbonaceous chondrites, obtained by us [5] and others, suggest that chondrule formation in the outer region of the inner solar system persisted for a much longer duration of ~3Ma. Plausible scenarios that may accommodate these observations relevant to the lifetime of an active solar nebula will be presented.

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Sulfur K-edge X-ray absorption spectroscopy as a tool to investigate microbial triggered sulfate reduction

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Investigation on the chemical states of sulfur is essential to characterize reaction products from microbial catalyzed neutralization of acidic mine waters and from laboratory experiments carried out with the iron and sulfate containing mineral jarosite ($KFe_3(SO_4)_2(OH)_6$)) exposed to sulfate reducing bacteria as a model system. With an element specific technique like the x-ray absorption spectroscopy (XAS), and therein from the near edge structure (XANES) information on the chemical binding form of sulfur can be obtained. XANES spectra at the sulfur K edge (around 2.48 keV) have been recorded at the XAS beamline of the synchrotron radiation source ANKA at the Forschungszentrum Karslruhe.

Due to the oxidation of metal sulfides (e.g. FeS_2) in coal mining sites metal ions and sulfuric acid are released in the adjacent waters. Thus, the acidic pit lakes that form in abandoned mining sites are an environmental hazard. A stimulation of sulfate reducing bacteria (SRBs) at the sediment water interface might act as a starting point to neutralize such lakes by transforming dissolved iron, metal and sulfate ions as well as the iron sulfate minerals of the lake sediment (e.g. jarosite) back into iron sulfides. Analysis of the sulfur K edge XANES shows in near surface samples of the sediment that was locally covered with calcium carbonate and organic carbon to increase bacterial activity reduced sulfur species (monosulfide). To understand the processes at the sediment water interface synthetic jarosite has been exposed to SRBs in the laboratory. Resonances in the spectra were assigned to monosulfide and disulfide sulfur besides the sulfate of the remaining reactant jarosite. Re-oxidation experiments indicate a similar behavior as for the lake sediments: the decrease of monosulfides to sulfur and to sulfate (Göttlicher and Mangold, 2005).

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A synchrotron radiation laboratory for environmental studies

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Samples required to solve Earth and environmental questions are often complex (e.g., weathered minerals and rocks, contaminated soils, lake and dump sediments). They consist of mixtures of mineral phases (often with micrometer particle sizes), microbes, and in some cases living tissues or are only available in scarce amounts of tiny particles (exhaust particles, precipitations in extreme environments). Elemental distribution, spatially resolved chemical speciation and mineral phase identification are helpful to uncover relationships between mineral phases, main and trace elements and finally to comprehensively understand natural and anthropogenic affected systems. Such problems can be addressed by a combination of microfocused synchrotron X-ray techniques as they have been setup with the Synchrotron Radiation Laboratory for Environmental Studies at ANKA. The lab consists of a microfocus X-ray beamline (SUL-X) that enable elemental mapping using X-ray fluorescence analysis (XRF), chemical speciation with X-ray absorption spectroscopy (XAS) and mineral phase determination by X-ray diffraction (XRD), successively at the same sample position. Moreover, the laboratory is supplemented with an infrared microscope (SUL-IR) at an edge radiation IR beamline.

First measurements during the commissioning period of SUL-X comprise localization and speciation of arsenic in natural iron minerals for water treatment and in weathering rims of sulfides in tailing impoundments by microfocused XRF analysis and X-ray absorption near edge structure (μ-XANES) spectroscopy. Selected area XRD has been used to identify mineral formations in sea water ice. μ-XRD and μ-XANES spectroscopy is applied to characterize lead in human bone junctions.

To meet the demand of speciation of low Z elements like Al, Si, P, S for environmental questions, it is planned to offer XAS at energies down to the Al K edge (1.5keV).

Microstrain and structural defects in the magnesian calcite skeleton of the Crown of Thorns starfish

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Sea stars have a magnesium calcite $(Ca_{1-x}Mg_xCO_3)$ skeleton made up of small ossicles which form an open meshwork supporting the body. In spite of their spongy morphology, the skeletal parts are single crystals as in other echinoderms (sea urchins, sea lilies, sea cucumbers and brittle stars). The skeletons are metastable formations as their composition often lies within the miscibility gap between calcite and dolomite. The Crown of Thorns starfish (CoT) was chosen for this x-ray diffraction study for its extraordinary high magnesium content of x = 0.17. The name is for the large number of long spikes. The high Mg content indicates an average water temperature of the habitat of about 29°C.

The x-ray powder reflections of CoT are slightly broadened with respect to those of quartz which was used as internal standard. A Williamson Hall plot indicates that the broadening is almost entirely due to microscopic strain caused by lattice imperfections rather than to small crystallite size. Annealing experiments suggest that the microstrain can only partly be explained by the different sizes of Mg^{2+} and Ca^{2+} cations incorporated in the calcite lattice. A single crystal structure refinement revealed the presence of vacancies on cation sites and misoriented CO_3 groups.

After annealing at 300°C, the appearance of few weak extra reflections indicate the beginning of the exsolution of high-magnesium calcite to low-magnesium calcite and calcian dolomite.

Annealing at lower temperatures (100 - 200°C) causes some changes of the microstructure which show up in the diffraction patterns. The lattice parameters expand slightly on increasing temperature of the heat treatment [1]. Simultaneously, the broadening of the x-ray powder reflections is reduced indicating less microstrain. Single crystal structure refinements show a reduction of vacancies and smaller atomic displacement parameters suggesting some healing of structural defects.

Annealing at about 250°C, however, causes an increase of the reflection broadening indicating larger microstrain introduced by newly formed lattice imperfections. Additional weak diffuse intensity was found close to the strongest reflections which can be ascribed to Huang scattering caused by the occupation of interstitial lattice sites. The formation of interstitials seems to be an intermediate step before at higher temperatures unmixing of the solid solution begins.

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Mobile fission and activation products in nuclear waste disposal

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When disposing nuclear waste in clay formations it is expected that the most radiotoxic elements like Pu, Np or Am do move only few centimetres to meters before they decay. Only a few radionuclides are able to reach biossphere and contribute to their long-term exposure risks, mainly ^{129}I, ^{36}Cl, ^{79}Se and in some cases ^{14}C and ^{99}Tc, whatever the scenario considered. The recent OECD/NEA cosponsored international MOFAP workshop focussed on transport and chemical behaviour of these less toxic radionuclides. New research themes have been addressed, such as how to translate molecular level information to large migration distances. Diffusion studies need to face mineralogical heterogeneities over tens to hundreds of meters. The large volume of traversed rock will provide so many retention sites that despite weak retention, even theses "mobile" nuclides may show significant retardation. The question however has been posed how to measure reliably very low retention parameters. Additionally, the radioactivity of some of the nuclides in the waste is so low that sophisticated techniques must be employed to measure them. An important issue is whether redox states or organic/inorganic speciation change from its initial state at the moment of release from the waste during long term contact with surfaces, hydrogen saturated environments etc.

Changes in soil reactive aluminium fractions following logging in podzols of British Columbia, Canada

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The potential for aluminium stress in ecosystems

Al is the 3rd most abundant crustal element, and in soluble forms is toxic to most organisms. The potential for acidic soils to be Al toxic is considerable. Ecosystems stressed by human interventions such as forest harvesting are particularly at risk.

This study investigates the effects of clear-cut logging on soil reactive Al fractions, including exchangeable Al (Al_{exch}), organically bound Al (Al_{org}), and Al associated with poorly crystalline minerals. The study soils are humo-ferric podzols located in the coastal mountains of southern British Columbia, Canada. These soils are strongly acidic and are at risk for Al stress. We collected soil samples from undisturbed plots (control), and compared them to samples from neighbouring plots that were clear-cut 1 to 15 years prior to sampling.

Results and discussion

Al_{exch} and Al_{org} are influenced similarly by logging. These Al pools are unaffected in plots logged 1 - 2 years ago, show an increase in plots logged 3 - 10 years ago, then decrease to control levels or below at 12 - 15 years after logging. This pattern matches closely the observed variation in the organic matter content. Organic matter provides exchange sites as well as sites for specific Al adsorption.

The increase in Al_{exch} is mitigated by a concomitant increase in exchangeable calcium. The Ca/Al ratio, a valuable ecological indicator used for the identification of the risk of adverse effects due to Al stress, was remarkably constant in control and logged plots.

Poorly crystalline mineral fractions consist mainly in imogolite-type material (ITM). Control soils average 23g/kg ITM in the B and C horizons. Logged soils exhibit highly variable ITM content, indicating a possible disruption of the podzolization process. With an Al/Si ratio around 2, ITM stores a significant fraction of the reactive Al in these soils.

Conclusion

All reactive Al pools in these soils are affected by logging. The impacts of these changes on the ecosystem are under investigation.

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Modelling of denitrification plumes induced by organic matter injection in aquifers

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Injection of organic matter can be an effective method for the remediation of nitrate-polluted aquifers. Microbial activity mediates the reduction of nitrate to N_2 by organic matter what can be exemplified by the following reaction:

$$5CH_2O + 4NO_3^- \Rightarrow N_2 + HCO_3^- + H^+ + H_2O$$
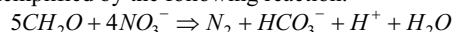
Nitrate pollution is of special concern in many areas of Catalonia (NE Spain). Although the accepted limit for drinking waters is 50 mg·L^{-1}, many aquifers in the region contains $[NO_3^-] > 75$ mg·L^{-1}, reaching in some cases up to 400 mg·L^{-1}. The Catalan Water Agency is presently designing an *in situ* experiment of organic matter-doped water injection in a selected aquifer with high nitrate concentration (~75 mg·L^{-1} NO_3^-). The extent and intensity of an aquifer denitrification plume is controlled by geochemical and hydrological parameters and variables (initial injected organic matter concentration, aquifer redox conditions, hydraulic conductivity, dispersivity and porosity).

The denitrifying capacity of the selected aquifer under study was tested in batch experiments in laboratory. From these experiments, a rate law of denitrification was determined and implemented in a series of 3-D reactive transport simulations aimed at selecting the optimal injection conditions, namely the injection rate of the reactive solution, organic matter concentration and injection pulse frequency.. Main parameters controlling the rate law were initial nitrate content, organic matter concentration and temperature.

In the numerical simulations, the total mass of organic matter to be injected (1.74 Kg$_{CH2O}$·day^{-1}) and total injection time (23 days) were kept constant while different organic matter concentrations and water injection rates were considered. The results show that solutions with organic matter concentration higher than 80 mg·L^{-1} at injection rates from 5000 to 20,000 L·day^{-1} generate a durable denitrification plume (>50 days under the maximum limit of nitrate concentration). Injection of water with lower CH_2O concentrations and higher injection rates leads to larger plumes but with lower denitrification intensity. The in situ test will also characterise aquifer properties such as depth-related redox conditions and the aquifer parameters given that the injection rate and the extent of the denitrification plume does not only depend on the geochemical variables but also on the ground water velocity.

U-series isotopes in suspended sediments of the Himalayan rivers

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Geochemical analysis of river sediments allows to study and quantify the parameters which control erosion and weathering processes at the scale of the watershed. In particular, ^{238}U-^{234}U-^{230}Th-^{226}Ra disequilibria are useful in supplying constraints on the time-scales of erosion and weathering processes (Granet *et al*., subm.; Chabaux *et al.*, 2003).

Previous studies were carried out on different kind of sediments : bedloads and river bank sediments (i.e. Granet *et al*., subm.), and suspended materials (i.e. Dosseto *et al.*, 2006). These works highlight quite different U-Th-Ra values for coarse sediments and suspended materials, which still need to be explained in order to propose robust time-scales of erosion and weathering processes.

Here we analysed U-Th-Ra disequilibria for all the solid phases carried by the Ganges river and its tributaries to understand the relationships among the different kind of sediments : river coarse sediments (Granet *et al*., subm.) and suspended materials sampled at different depths in the water column.

U-Th-Ra analyses of samples collected at the same location highlight a wide range of values from the coarse sediments to the surface suspended materials. The chemical heterogeneity is explained by the fact that the U-Th-Ra composition of the suspended materials is the result of a mixing between coarse sediments and fine materials collected at the same sampling location but which have different origins at the scale of the Ganges basin. The data allow to conclude that the fine materials originate from the Ganges alluvial plain where they have been trapped before to be reworked and carried by the rivers.

The chemical differences observed between suspended materials and river coarse sediments are due to their different origin and history. This certainly accounts for the different time-scales of transfer proposed for these solid phases : long times of about 100's ka for the coarse sediments (Granet *et al.*, subm), and, in agreement with the mixing scenario, short times for the suspended materials.

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Time-space migration of melting within the E-Atlantic plume and magmatism in Portugal: U-Pb ages and Pb-Sr-Hf isotopes

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To examine time-space relations between gabbroic to granitic alkaline magmatism in Portugal and seamount formation in the central east Atlantic region we have undertaken (1) U-Pb dating on zircon and titanite, (2) U-Pb and Rb-Sr isotope analyses on grain-by-grains selected feldspars and (3) Hf isotope analyses of the dated zircons. Ages are 68.9 ± 0.3 (2σ) and 70.0 ± 1.0 Ma for the Monchique complex, and 77.2 ± 0.2, 77.1 ± 0.4 and 75.8 ± 0.2 Ma for the Sines massif. For the Sintra magmatic complex four ages of 82.1 ± 0.1, 83.4 ± 0.7, 80.2 ± 0.6, and 81.7 ± 0.4 Ma are obtained. An older age of 88.2 ± 0.5 Ma is defined for the Ribamar complex. These ages define a period of at least 19 million years for alkaline magmatism showing a systematic increase in ages from south to north. For intrusional-subvolcanic rocks exposes more than 100 km to the north, much older ages of 146.5 ± 1.6, 142.3 ± 1.0, and 145.3 ± 1.4 Ma were determined.

Corrected for in-situ decay of U and Rb (isotope dilution) Pb_i in the Cretaceous rocks lie at 18.522-19.299 for $^{206}Pb/^{204}Pb$; at 15.555-16.007 for $^{207}Pb/^{204}Pb$, and at 38.482-39.350 for $^{208}Pb/^{204}Pb$, and Sr_i are 0.70274 to 0.70481. For Hf isotopes, εHf_i range from +4.3 to +9.6. Most sources are less radiogenic in ^{206}Pb than the Cretaceous seamounts but they partly overlap with data from younger seamounts and the Madeira Archipelago. Examined in the Pb_i vs. εHf_i correlation diagrams all data plot in or adjacent to the field of worldwide OIB sources, being significantly different from any Atlantic MORB source. Cretaceous anorogenic alkaline magmatism in Portugal therefore requires melting of OIB-like mantle sources possibly followed by melting of the Iberian subcontinental mantle, as well as small contributions from old crust. The large spectra of lithologies seems to reflect differences in degrees of melting in possibly both, the plume and the subcontinental mantle. Emplacement of the 88 to 69 Ma alkaline complexes including the 77 Ma old Ormonde seamount is younger than Cretaceous seamount formation along the continent-ocean transition in the central east Atlantic. On the other hand, it is much older than Oligo-Miocene and Quaternary seamount emplacement. This pattern allows to establish that melting within the plume migrated in time from West (104-81 Ma) to East (88-69 Ma) and South (< 69 Ma).

Lithium incorporation in olivine

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The relative concentrations of the two stable isotopes of lithium are increasingly being used to investigate chemical homogeneity and evolution of the upper mantle. The principal host for lithium in the mantle is olivine, but how univalent species, such as Li and Na, are incorporated into the crystal structure remains poorly understood. Here, we describe the results of isobaric crystal-melt partitioning experiments which, together with thermodynamic modelling, provide insight into the mechanisms of incorporation of Li in forsterite and natural olivine of mantle composition.

The results of partitioning experiments conducted on end-member forsterite doped with varying concentrations of lithium and trivalent cations show that the dominant substitution mechanism depends strongly on the concentrations of dopant elements. At relatively high concentrations (>20 ppm Li in the crystal), lithium is principally incorporated into near end member forsterite via coupled substitution with trivalent cations such as Al and Fe^{3+}. At <20 ppm Li in the crystal, however, there is no correlation between Li partitioning and trivalent element concentration and results indicate charge-balance via vacancy or interstitial defect formation.

The lithium contents of natural olivine from the spinel stability field were measured using LA-ICPMS. The amount of Li in olivine is low (<5 ppm) and, unlike Na, does not correlate with the concentration of any trivalent cation species. We therefore conduced a series of additional experiments in order to investigate Li incorporation in natural, Fe-bearing olivine. In these experiments, crystals were grown at 1 atm from a natural basanite melt, at a range of oxygen fugacities. The results demonstrate that the partitioning of lithium between iron-bearing olivine (approximately Fo89) and melt is strongly dependent on oxygen fugacity (fO_2). The concentrations of lithium in mineral-melt pairs from our experiments show that $D_{Li}^{olivine-melt}$ decreases from 0.3 at IW to 0.15 at NNO. This negative dependence on fO_2 suggests that lithium is incorporated into Fe-bearing olivine either through formation of oxygen vacancies or coupled to tetrahedral Fe^{2+}. The consequences are that partitioning and diffusion of Li in natural materials is strongly dependent on the activities of major components in the medium.

A chondritic and nonchondritic Earth: What would the dynamicists say?

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The question of the origin of water on Earth is as pure as SMOW: it can be reduced to endogenic or an exogenic sources, however the reduction problem is anything but simple. This complex question must probed via theoretical, physical, isotopic, and geochemical arguments, each of which require highly specialized skills. Many of the physical arguments can be numerically probed via n-body simulations that build terrestrial planets from smaller bodies in the inner solar system during its formation period, while many of the isotopic and geochemical arguments can be explored via sample collections and remote measurements of terrestrial and extraterrestrial materials. To properly address the question of the origin of water on Earth requires that each of these approaches use the other approach as a constraint.

For example, upon building their planets, the dynamicists will negate or affirm their simulated planets with constraints including (D/H) ratios, water abundances, noble gas isotopic ratios and abundances, and nitrogen, oxygen, and HSE isotopic compositions. And, upon collecting their samples, the geochemists will negate or affirm the samples' origins using physical models of solar nebula gas temperatures, time for core formation, dates of chondrules and zirons and mixes of solar elements to construct a body with plausible elemental compositions. However, their tasks are not finished, until a synthesis of the two approaches is attempted.

In this work I will present the second approach from the geochemical angle with a first synthesis between the two approaches. While a chondritic Earth is often assumed by geochemists, the implications for a nonchondritic Earth are: 1) no depleted mantle reservoirs, 2) no geochemical paradoxes, 3) the Earth's mantle is entirely degassed, 4) an explanation of the early appearance of a depleted mantle, and 5) a solution of the heat-^{4}He paradox [1]. Which type of Earth better meets the dynamical constraints?

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2.7-2.6 Ga Archaean ecology determined by microbial activities: A view from C and S isotopes

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The well-preserved Belingwe Greenstone Belt (2.7-2.6Ga) in Southern Zimbabwe was deposited in a sub-continental basin upon a basement gneiss. The isotopic study from drill-cores was based on clastic sedimentary units of two formations: Manjeri Fm. (2.7Ga) and Cheshire Fm. (2.6Ga). The most interesting sections of the Manjeri Fm. are two carbon- and sulphur-rich black shale layers, Shavi and Jimmy Members, with reduced carbon contents up to 20wt%. The very wide δ^{34}S range of 40‰ obtained on pyrite separates (from –23.7 to +16.7‰) and the similarly wide δ^{13}C range for reduced carbon of nearly 32‰ (from –38.4 to –7.0‰) indicate primary bacterial matter. Such variations are in favour of biological fractionation that indicate various co-existing metabolic pathways: an oxygenic photosynthesis signature and anoxygenic processes. There is also strong evidence for sulphate-reducing activity and even for S-oxidizers in various sections of the core. Some results associated with δ^{13}C measured in carbonate clumps suggest the existence of a methane seep environment, emphazing that complex microbial communities existed at 2.7Ga, based on well represented C and S biological cycles.

The Jimmy Member has been sampled from three different cores. The isotopic results suggest variations in the biological activities between the three localities. There is evidence of changing processes in the microbial mats, which allows an overview of the ecology of the Belingwe basin at this specific period. In fact, these changes are caused by changing biotopes in the environment, most likely due to the subsidence of the basin shifting sedimentation for shallow water to a deeper setting.

In the Cheshire black shales, δ^{13}C with values between –44 and –32‰ suggest that methanogenic and even methanotrophic processes were present in the basin too. In addition to this study, δ^{13}C for carbonate and reduced carbon have been measured on different stromatolitic sequences (Abell et al., 1985) from the two formations. The isotopic fractionations obtained are in favour of the Rubisco I signature indicating cyanobacterial activity.

All these information allow the re-constitution of the ecosystems that were present between 2.7 and 2.6Ga in the Belingwe basin. Multiple biological activities and various ecologies were needed to colonize the entire planet and to allow the evolution of the Archaean life.

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Natural pigments as enamel opacifiers on ancient glass: Raman study of lazurite colour decoration on 1st to 2nd century glass vessels from Lubieszewo (Lübsow), Poland

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Glass vessels decorated with colourful designs either by application of pigments or a low melting coloured glass flux were highly estimated by the Germanic population along the Northern and Eastern borders of the Roman Empire in the 1st and 2nd century AD. Despite the fact that a number of splendid examples with depictions of birds, fishes and plants has survived in high ranking tombs of the barbaric elite, investigations either of the glass composition or the decoration technique employed are still quite limited.

In the case of the Lübsow glasses the basic pattern is scratched on the glass body before the coloured glass flux layers carrying the pigments are applied. The presence of lazurite grains as colouring and opacifying agent was confirmed by Raman micro-spectrometry of a pale grey ornament with a more vivid blue colour visible from the back side of the sherd.

The use of Lapis Lazuli as decorative inlay or as pigment for wall paintings in Mesopotamia, Egypt, Greece and the Roman Empire is a well known fact (see e.g. Derakhshani 1999). The as yet earliest evidence for its application in a high temperature process seems to fall into the 13th century with a lazurite rich slip under a cobalt glaze on an Iranian ceramic ewer (Colomban 2003) and the use for blue colours on enamelled transparent glass vessels (Freestone & Stapleton 1998). The observation that lazurite was used as a pigment in a glass flux on vessels from a Roman period context sheds a new light on the development of the manufacturing techniques of enamelled glasses in antiquity.

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The "Mg-sursassite" story

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The high-pressure phase $Mg_5Al_5Si_6O_{21}(OH)_7$ named MgMgAl-pumpellyite in analogy to the phase MgAl-pumpellyite (Schiffman & Liou 1980) was identified in experiments in the system MgO-Al_2O_3-SiO_2-H_2O for the first time (Schreyer *et al*. 1986). Due to its close chemical similarity to pyrope and the high-pressure, low-temperature stability delineated by Fockenberg (1998) up to 10 GPa, this phase was proposed to be an important water reservoir in cold subducting slabs (e.g. Schreyer *et al*. 1991; Fockenberg 1998). Gottschalk *et al*. (2000) found strong evidence that $Mg_5Al_5Si_6O_{21}(OH)_7$ is isostructural to natural sursassite, $Mn_4Al_6Si_6O_{22}(OH)_6$. Therefore, they suggested calling this high-pressure phase Mg-sursassite.

Calorimetric and *P-V-T* data for Mg-sursassite have been obtained by Grevel *et al*. (2001). The enthalpy of drop-solution was measured by high-temperature oxide melt calorimetry using lead borate at $T = 700$ °C as solvent. The resulting values were used to calculate the enthalpy of formation from different thermodynamic data sets; they range from -13892.2 kJ mol^{-1} to -13927.9 kJ mol^{-1} (formation from the elements). The heat capacity of the phase has been measured from $T = 50$ °C to $T = 500$ °C by differential scanning calorimetry. A Berman & Brown (1985) type four-term equation represents the heat capacity over the entire temperature range to within the experimental uncertainty: $C_P (T) = (1571.104 - 10560.89 \times T^{-0.5} - 26217890.0 \times T^{-2} + 1798861000.0 \times T^{-3})$ J K^{-1}mol^{-1} (T in K).

The *P-V-T* behaviour of Mg-sursassite has been determined under high pressures and high temperatures up to 8 GPa and 800 °C using a MAX 80 cubic anvil high-pressure apparatus. By fitting a Birch-Murnaghan EOS to the data, the bulk modulus was determined as 116.0 ± 1.3 GPa, ($K' = 4$), $V_{T,0} = 446.49$ Å^3 exp [$\int (0.33 \pm 0.05) \times 10^{-4} + (0.65 \pm 0.85) \times 10^{-8} T$ dT], $(\partial K_T / \partial T)_P = -0.011 \pm 0.004$ GPa K^{-1}. The thermodynamic data obtained are consistent with the phase equilibrium data (Fockenberg 1998) and included into the internally consistent dataset of Grevel (2004); the best agreement was obtained with $\Delta_f H^0_{298} = -13907.33$ kJmol^{-1}, and $S^0_{298} = 608.39$ JK^{-1} mol^{-1}.

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Significance of Biomarkers for P/T and F/F Mass Extinctions

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The most significant pulses of evolution throughout Earth's history have coincided with abrupt extinction events (e.g. Benton & Twitchett 2003). The most pronounced extinction of the Phanerozoic occurred near to the Permian-Triassic (P/Tr) boundary. Many trigger mechanisms have been proposed for the P/Tr event and include bolide impact, Siberian flood basalt volcanism, ocean anoxia, H_2S emissions and catastrophic release of methane from the collapse of gas hydrates, all leading to the loss of many marine organisms and land plants. Biomarkers derived from pigments of photosynthetic green sulfur bacteria have been reported in sections from W. Australia and S. China, indicating the presence of toxic H_2S in the zone of light penetration (PZE) of the Tethys Ocean during the P/Tr extinction (Grice *et al.*, 2005). Similar observations were made in a section from W. Canada (Hays *et al.*, 2007) suggesting that the Panthalassic Ocean was also prone to periodic euxinia. Any H_2S reaching the atmosphere would have been both toxic and persistent (Kump *et al.*, 2005). The significance and value of biogeochemical markers for identifying changes at the P/Tr and F/F will be presented. In particular, the pervasiveness of PZE conditions and the origin and importance of the biomarker crocetane, generally associated with the anaerobic oxidation of methane, will also be presented.

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Amorphous components in the shell material of the brachiopod *Megerlia truncata*

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Brachiopods have existed throughout the phanerozoic and they developed shell materials employing the two principal mineral groups of hard biologic tissue: calcium carbonate and calcium phosphate, each with distinct hierarchical architecture [1, 2, 3]. We have observed a large domain filled with amorphous calcium carbonate in the shell of the modern brachiopod *Megerlia Truncata* by transmission electron microscopy. The domain has the typical outer shape and size of calcite crystals composing the fibrous secondary layer shell. It is adjacent to a large solid inclusion incorporated into the shell, suggesting that the amorphous material is related to a repair mechanism. The fibres of the secondary shell layer are surrounded by an an organic sheath. Along the innermost segment of the secondary layer, in addition to the organic sheaths, thick organic membranes are present. The amorphous domain is located between two thick organic membranes. In the outer nanocrystalline (primary) layer we do not observe any organic material between the crystallites. Under TEM imaging conditions the amorphous carbonate crystallized in situ to vaterite. Our observations indicate that brachiopod shell formation may occur via an amorphous calcium carbonate precursor that is produced in an initial stage prior to the crystallization of calcite.

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Non-monotonic scenarios for the Earth's thermal history

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Expected variations of heat loss out of the Earth's mantle with the cycle of aggregation and separation of supercontinents and the consequent variations of the wavelength of mantle flow are important, of the order of 20 TW on a timescale of a few hundreds million years [Grigné *et al.* 2005]. Monotonic models of planetary thermal evolution do not account for those variations and thus, may not be relevant for the Earth. The observed variations obtained in numerical models of mantle convection including continents are presented.

On a longer timescale, an event that may influence the heat loss of a terrestrial planet in a more dramatic way is the possible cessation of plate tectonics [e.g. Lenardic *et al.*, 2004, Sleep 2000]. This possibility is studied here using models of thermal convection including a temperature-dependent viscosity and plastic yielding, which leads to either a stagnant lid or a plate-like regime, depending on the chosen parameters for plastic yielding, on the vigour of convection, on the thermal state of the mantle and on the geometry of the flow. We discuss the consequences of switching between the two regimes on the thermal state of the mantle, particularly on the temperature and heat flux at the core-mantle boundary, and on the thermal evolution of terrestrial planets.

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The non-existence of the SEP noble gas component – Implications for geo- and cosmochemistry from Genesis samples

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Dust grains from the lunar regolith appear to contain a solar noble gas component istopically heavier than the solar wind that is trapped at larger depths. This component was attributed to solar particles implanted at considerably higher energies than the solar wind and dubbed "SEP" for Solar Energetic Particles. Though it has been impossible to reconcile the high apparent abundance of the "SEP" component in lunar samples with the very low flux of solar energetic particles measured in-situ in space, the "SEP" component also found wide acceptance for the interpretation of N and O data in cosmo- and geochemistry.

Ne and Ar data from a metallic glass exposed on the Genesis mission now have clarified this conundrum. The isotopic and elemental depth profiles in the glass are very similar to those predicted for a solar wind uniform in composition implanted with the velocity distribution as measured by Genesis instruments. Thus, the gases at larger depths do not represent an isotopically distinct component but are solar wind particles that got fractionated with implantation depth as a function of their mass (Grimberg *et al.*, 2006).

In this contribution we will discuss some implications of this finding for noble gas geo- and cosmochemistry. The interpretation of solar Ne in the Earth's mantle being due to accretion of grains irradiated by an early solar corpuscular radiation (Trieloff *et al.*, 2000) may be maintained, except that the observed Ne composition in this case would not be a result of large contributions of "SEP"-Ne but rather has to be implantation-fractionated SW-Ne. Similarly, the inferred isotopic composition of solar O in lunar dust reported by Hashizume and Chaussidon (2005) with a $\Delta^{17}O$ value less than -20‰ needs not to be revised, though the O measured by these authors has now to be viewed as fractionated SW-O rather than as "SEP"-O. On the other hand, the proposed inverse trend between the isotopic composition of Ne and N from SW to "SEP" (Mathew *et al.*, 1998) needs to be reinterpreted in the light of our results.

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Modelling of radium-barium sulphate co-precipitation in the near field of a HLNW repository

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The solubility limit of radium is one of the main uncertainties remaining in the safety assessment of high-level nuclear waste repositories. Previous evaluations have commonly considered $RaSO_4$ as the solubility limiting phase, although observations in Nature indicate that this phase never occurs. Since the pionnering laboratory work of Germann (1921) and Doerner and Hoskins (1925), which showed a readily incorporation of radium into the barium sulphate (barite) lattice, most studies have concluded that the fate of radium in waters is intimately linked to barite precipitation. Both radium and barium are present in spent nuclear fuel,. Most of the barium will be created during fuel irradiation, but some will also be generated shortly after the fuel is discharged from the reactor through decay of the short-lived isotopes of caesium, namely ^{134}Cs and ^{137}Cs. About 5 kg of Ba are estimated for each waste canister (SKB, 2006). On the other hand, radium is progressively generated by U-Th isotope decay chain, and maximum Ra inventory is going to be produced from the spent fuel after 100,000 years. The coexistence of both, Ba and Ra, in the fuel makes feasible the formation of $(Ba,Ra)SO_4$ solid solution, and, therefore, there is a great potential for reducing the calculated releases of ^{226}Ra if co-precipitation effects are considered. These solid solution would occur at the interface between canister and clay-based barrier when, as a consequence of failure of canister integrity, a sulphate-rich water from the barrier leaches Ba and Ra from the spent fuel. In this conceptual model, the supply of sulphate is a key parameter to ensure $(Ba,Ra)SO_4$ formation. Calcium sulphate is a common accessory mineral in many bentonite rocks used in the barriers, although it can be easily leached by inflowing groundwaters, especially in ice-melting water intrusion.

In this study, we have calculated the effect of solid solution formation on the radium solubility limit in wide ranges of radium, barium and sulphate concentrations. The results obtained show that radium solubility limit can be reduced up to 4-5 orders of magnitude, mainly in those cases in which initial barium concentration is higher.

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Single particle sampling and analysis

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The ability to sample and analyse individual particles is paramount for the determination of their sources, their distribution and to understand their interaction with the environment. Electromagnetic and thermophoretic sampler have been designed for collecting the ultrafine fraction (< 0.5PM) directly onto TEM grids. The results from numerical modelling of the deposition patterns and the sampling efficiency compared well with the experimentally determined performance of the samplers. Particle counts and chemical analysis (SEM, TEM) of individual particles sampled on a TEM grid can, therefore, easily be translated into quantitative information about the sampled aerosol.

Different sources of ultrafine particles have been studied using the new collectors. Particle emission from railway traffic and welding workplaces have been investigated by conventional EDS-based single particle analysis. Synchrotron based scanning transmission X-ray microscopy (STXM) and carbon(1s) near edge xray adsorption fine structure (NEXAFS) spectroscopy have been used to analyse soot particles produced by diesel engines and wood fires. First results show clear differences in the chemical structure of the particles from the two sources. NEXAFS may, therfore, be used as tool for the source apportionment of soot particles, but also to follow their evolution with time.

An improved single-step distillation of chromium-reducible sulfur

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The determination of elemental sulfur by chromium distillation is a controversial subject. Since elemental sulfur is an important intermediate in sulfur transformations in natural environments, a reliable method for quantitative recovery is required. Especially in the assessment of risks from acid sulfate soils a quantitative determination of all reduced inorganic sulfur compounds (RIS) is essential. In this field the chromium distillation has already been shown to be superior to other methods (e.g. Sullivan et al., 1999).

In the analysis of elemental sulfur Canfield et al. (1986) found a recovery of 92 % but did not specify any further the form of elemental sulfur deployed. Wieder et al. (1985) observed 94,4 % recovery by using powdered elemental sulfur but only in minor amounts. Fossing and Jørgensen (1989) and Kallmeyer et al. (2004) proved that the recovery of elemental sulfur is clearly limited. In their experiments only in dissolved state a quantitative recovery could be obtained. Neither granular nor colloidal sulfur showed recoveries >50%. Our experiments carried out with the procedure according to Canfield et al. (1986) yielded recoveries of less than 50% in the analysis of powdered elemental sulfur.

Our modified method provides recoveries >90% (mean value: 94 %) for powdered, colloidal and dissolved elemental sulfur up to at least 16 mg S (approx. 3,2% of a 0,5 g sample). Nevertheless all other reduced inorganic sulfur species are quantitatively recovered. The modified method is selective towards RIS. It does not affect organosulfur compounds or sulfates. The selectivity was verified with methionine, cystine, cysteine, taurine, gypsum and barite.

The obvious advantage of this method is the ensured quantitative recovery of elemental sulfur. Furthermore no additional toxic solvents, e.g. dimethylformamide (DMF) (Kallmeyer et al., 2004), are required. Besides that the selectivity of procedures involving DMF has not been tested with organosulfur compounds.

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Determining mineral solubilities at high pressures: A new method combining weight-loss and *in situ* approaches

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Although a fairly extensive dataset is now available on the solubility of minerals in aqueous fluids at high pressure and temperature, almost all of the data above 0.5 GPa have been obtained by *ex situ* quench methods in piston-cylinder apparatus. A few comparative studies between such indirect weight-loss techniques and direct disappearance-of-phase, *in situ* methods are available, but only for trace elements (e.g. Ayers and Watson, 1993; Audetat and Keppler, 2006; Tropper and Manning, 2005). The results show huge differences, which are not yet satisfactorily explained. Here we introduce a new approach for determining solubilities of dissolved components using a hydrothermal diamond anvil cell (HDAC). We propose to exploit the tendency of crystals to approach an idiomorphic habit during HDAC runs, as observed by Wang et al. (2004), and also in our own HDAC studies. By defining the habit of a crystal before the run, its changing geometry can be modeled at various stages of the experiment. Knowing its original volume and mass, absolute solubilities can be determined. By comparing masses at various PT conditions, relative changes in solubility can be calculated. Our specially designed HDAC (Burchard et al., 2003) allows fluid pressures up to 4.0 GPa to be reached. The results should allow a more fundamental and objective comparison between *in situ* and *ex situ* experiments. The initial focus is on quartz solubility in pure water, in order to assess the voluminous published data at hand, most of which has been obtained by *ex situ* methods. However, important rock-forming minerals such as feldspar and mica appear viable targets for this approach.

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Processes controlling the relationship between volcanic fronts and the subducting slab revisited

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Thus far a thorough understanding of the controls on the position of the arc volcanoes above the subducted slab has remained elusive. Recent work by England *et al.* (2004, *GJI*, **156**, 377) and Syracuse and Abers (2006, G^3, **7**, 5) explores global variations in depth to the slab below the volcanic front. England *et al*. find a systematic variation in depth to the slab, which they attribute to the product of the convergence rate of the slab and the angle of descent (Vsinδ). They conclude the downdip velocity (Vsinδ) likely controls the temperature structure in the wedge because as the downdip velocity increases, the rate at which hotter mantle is sucked into the nose of the mantle wedge increases. This observation, when combined with new experimental results on the H_2O-saturated melting of peridotite (Grove *et al.*, 2006, *EPSL* **249**, 74), provides a model to explain the location of arcs above the subducted slab. Grove *et al*. found the vapor-saturated melting curve for peridotite has a negative slope. Therefore as pressure decreases, temperature increases and the minimum depth of melting is limited by the maximum temperature in the shallowest - hottest part of the wedge nose. Thus, the negative slope of the H_2O-saturated peridotite solidus controls the minimum depth where melting can occur. Following this model, as the downdip velocity decreases: 1) the depth to the hottest point on the wedge nose is increased, 2) the volcanic arc is shifted away from the trench and 3) the depth to the slab is increased. The H_2O-saturated phase relations also predict that there should be a maximum cut-off depth for hydrous flux melting at ~135 - 150 km depth because the hydrous phases (chlorite and serpentine) present in the mantle wedge above the slab and within the slab have dehydrated by this depth. Arc volcanoes >150 km above the slab are therefore likely the product of adiabatic decompression melting, not hydrous flux melting.

DuneXpress, *in situ* analysis of interstellar dust

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Interstellar grains are messengers through space and time from the remote sites in which they formed and traversed in their journeys. Born as stardust with the elemental and isotopic compositions characteristic of the cool atmospheres of giant stars or of novae and supernovae explosions, they are subsequently modified in the interstellar medium. Interplanetary dust represents more processed material from comets and asteroids at different stages of Solar System evolution. DuneXpress will provide the capability to inter-compare between epochs of our cosmological history and our planetary history, via the study of the compositional variation and differences between interplanetary and interstellar dust particles.

The key to this treasure is dust astronomy. Dust astronomy requires a dust telescope in space to detect particles while accurately distinguishing their origins via their interstellar and interplanetary trajectories. Trajectory sensors utilize the electric charge signals induced when charged dust grains fly through the detector. These sensors, in combination with state-of-the-art in-situ dust impact detectors, are capable of determining mass, speed, physical properties and the chemical composition of individual dust grains in space.

The detailed objectives of DuneXpress are: 1. Mapping the seasonal interstellar and interplanetary dust flow. 2. Identification of the chemical and isotopic classes of cosmic dust grains. 3. Determination of the size distribution of interstellar dust. 4. To study the differences between interplanetary dust of cometary and asteroidal origin.

The DuneXpress spacecraft will be placed in a halo orbit at the L2 libration point of the Sun-Earth system, outside the Earth's debris belts. The spacecraft is three-axes stabilized and provides pointing of the dust telescope to better than one degree. The payload consists of dust telescopes, dust cameras and a plasma monitor. The total sensitive area of the dust instruments will be 1 m^2. The newly developed dust telescope consists of a Dust Trajectory Sensor (DTS) and a Large-Area Mass Analyzer (LAMA). LAMA consists of an impact target of 0.1 m^2 sensitive area. It performs time-of-flight measurements of ions generated by hypervelocity dust impacts onto the target. The device employs a reflectron in order to reach a mass resolution $M/\Delta M \geq 150$.

The mission costs less than 100 M€ and could be launched as early as 2013.

Potential remobilization of phosphorus from acid mining lake sediments

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Introduction and methods

Natural maturation or artificial neutralization measures will lead to an accumulation of organic carbon (C_{org}) and phosphorus (P) in acid mining lakes. Concurrently, a reduction of Fe-imports into these lakes is foreseeable (Kleeberg and Grüneberg 2005).

Consequently, due to low redox potential and the neutral pH conditions in the sediment, reductive dissolution of Fe-hydroxides and the formation of sulfides might lead to P-remobilization and higher trophy.

This hypothesis was tested by studying the response of undisturbed sediment cores from the mining lake 117 (pelagic pH 3, age 35 a, z_{max} 14.4 m, Plessa mining area, Lusatia, Germany) to C_{org}- and P-additions. Glucose and dried *Chlorella* algae where added at rates between 0.2 and 3.5 g C m^{-2} d^{-1}.

Results

Only the columns with high sulfur (S) and relatively low Fe content (Fe:S ratio molar 1.4 – 2.0) showed P release with a flux between 0.15 and 0.46 mg m^{-2} d^{-1}, which is in a range comparable to oligotrophic lakes. The resulting concentration of soluble reactive P (SRP) in the pore water was approximately calculated in adsorption equilibrium with the fraction of Fe which is not immobilized as FeS using PHREEQC (Parkhurst and Appelo 1999). Vivianite formation is probably inhibited as high SRP-concentrations in the pore water up to 0,63 mg l^{-1} can not be explained in equilibrium with Vivianite.

Column experiments proved that P-sorption capacity becomes very low (< 1 mg P m^{-2} d^{-1}) under the influence of FeS_x-formation in the sediment and without constant supply of $Fe(OH)_3$, and that a mobilization of sediment P is possible despite high Fe content. The future P-sorption capacity might be approximated from the ratio of Fe- and S-input into the lake, provided that the supply of C_{org} is adequate for intensive sulfate reduction.

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Estimation of ferromanganese concretions growth rates using [210]Pb

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The present investigations are devoted to dating of ferromanganese concretions from Gulf of Finland using [210]Pb. About 90% of ^{210}Pb detected in the concretions are generated directly inside concretions as a result of [222]Rn decay formed from [226]Ra. The content of [226]Ra in the concretions are 10-50 times higher than in all types of bottom sediments irrespective of the morphology of the concretions (Grigoriev *et al.*, 2004).

For the study of ^{210}Pb concentrations one spheroidal concretion (20 mm in diameter) sampled in the eastern Gulf of Finland was selected. Four probes for ^{210}Pb determination were sampled: 1 – from the centre of the concretion (distance from the centre 0-2.5 mm); 2 – 2.5-5 mm; 3 – 5-8 mm; 4 – 8-9 mm. Analysis of ^{210}Pb concentrations was fulfilled in the Center of Isotopic Research of VSEGEI. The radioactive decay spectra of ^{210}Pb and its daughter elements were detected with liquid-scintillation spectrometer Quantulus 1220.

The first model does not take into account [222]Rn emanation. Composing equations set and solving it we got the minimal value of concretion age 670±50 yr. Accordingly the rate of concretions radial growth is within the range 0.013 – 0.042 mm/yr.

For the second model we tried to take into account [222]Rn emanation. For this purpose we applied parameter φ, which defines emanation process. After solution of the equations set we obtained the age of studied spheroidal concretion is within the range 260 – 490 yr or its radial growth rate is within the range 0.018-0.034 mm/yr.

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Remobilisation experiment of sulphides from massive Sulphide ore at 350°C and a differential stress without exotic fluid

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The sample for the experiment is massive sulphide ore free of intense deformation textures, and is composed mainly of pyrite (32%), pyrrhotite (8%), chalcopyrite (9%), sphalerite (7%), quartz (25%) and silicates (14%). Fluid inclusions in quartz have salinities in the range of 15.96~22.98 wt% NaCl equiv.

A sample cylinder 17 mm in diameter and 40 mm in length was dried in an oven at 100°C for 24 hours before being mounted in a 3-axes rock stress machine with piston-cylinder equipment. After the experiment for 13 hours at temperature of 350°C, confining pressure of 414 MPa and axial pressure of 1276 MPa, the sample was cooled at room temperatures for 24 hours.

In the experimental product, pyrite has been intensely cataclastically deformed, resulting in numerous cracks and angular fragments. By contrast, pyrrhotite, chalcopyrite, and sphalerite are dominated by plastic deformation. Remobilised chalcopyrite and pyrrhotite occur as veinlets cutting pyrite porphyroclasts or as cementing materials of pyrite fragments, whereas remobilised sphalerite is only seen in minor amount in a few veinlets. The sulphides in the veinlets and breccia metrix are not connected to the same minerals outside the pyrite porphyroclast, indicating that remobilisation was not in solid state due to mineral plasticity, but was driven by fluid. Under transmitted light, no dewatering textures of hydrous minerals have been observed, indicating that, the fluid for sulphide remobilisation in this experiment was derived mainly by breakdown of fluid inclusions.

The results of this experiment have lead to the following conclusions: 1) Deformation without exotic fluid can induce remobilisation of ore components. 2) Apart from metamorphic dewatering of hydrous minerals, breakdown of fluid inclusions due to deformation is capable to provide sufficient fluid for metal remobilisation. 3) Deformed pyrite is the best substrate for the precipitation of remobilised sulphides. 4) Sphalerite shows less strong tendency to remobilise than chalcopyrite under condition of the present experiment.

Petrography and Geochemistry Features of the Yoncayolu Metamorphics in Erzincan, NE Turkey

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The study area is located of between transitional zone Pontide and Anatolide tectonic units, on the eastern of Erzincan (NE, Turkey). The aim of this study to explain mineralogy, pertography and geochemical characteristics of Yoncayolu Metamorphics. Permo-Triassic aged these metamorphics extend almost parallel to North Anatolian Fault and have lenses of phyllite, schist, calc-schist, quartzite, orthogneiss and metabasics of very-low grade, low-grade and often medium grade metamorphic rocks. These metamorphics are overlaid by Lias-Dogger aged Cayderesi Limestones. The Refahiye Ophiolite Melange cover both of these units tectonically [1].

In the study area, sericite+chlorite+quartz±muscovite-mineral assemblaged schists, amphibole+albite+K-feldspar+quartz±chlorite-mineral assemblaged gneisses, and quartz+sericite+calcite±chlorite-mineral assemblaged calc-schist are determined. Metabasics are characterized with light schistosity rather than formation of new minerals. Metamorphics are cut often by quartz veins and dense epidotization is observed at their contacts.

Metamorphics have a composition of 50-77% SiO_2, 9-21% Al_2O_3, 2-12% Fe_2O_3, 1-7% MgO, 2-5% Na_2O, 0,1-2,2% K_2O. Comparing to SiO_2 with major element values, a negative correlation between SiO_2-Al_2O_3, SiO_2-Fe_2O_3, SiO_2-MgO, SiO_2-CaO are seen whereas, there is a positive correlation between SiO_2-Na_2O. Similarly a negative correlation exist between SiO_2-Ga, SiO_2-Sr, SiO_2-Ni and a positive correlation between SiO_2-Nb, SiO_2-Zr, SiO_2-Y. Phyllite, schist and calc-silicate rocks fall in the within the calc-alcaline field on an AFM plot but metabasic rocks fall within the tholeiitic field. On the Ni-Zr/TiO_2 diagram all of the samples values point a igneous origin [2]. On the diagrams a positive correlation of K_2O versus Th, Ba, Rb are exists that are related to clay minerals within metamorphics.

Metamorphics exhibit an increase from very low grade to medium grade metamorphism along south to north.

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Phosphates from of the Martian meteorites: A cathodoluminescence spectroscopical overview

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Introduction

The purpose of this study is to identify and microcharacterize the phosphates in Martian meteorites.

Samples and Experimental Procedures

Standard polished geological thin sections were prepared from the Nakhla, ALH84001 and Y-000593 nakhlites for WDS analysis and CL spectral investigation. Details on the CL equipments, methods, sample preparation and samples can be found in [1-3].

Discussion of results

Various phosphates such as β-Ca-phosphate (ALH84001), chloroapatite (Nakhla) and apatite (Y-000593-nakhlite) have been identified in these samples (Fig. 1), indicating the mineralogical information on the fluid-rock-atmospheric interactions in the Martian environment   s.

Sample	CL spectra (nm)	Phosphate	Ref.
ALH84001 (#3734,373 83739 fragm.)	350: Ce, La 478: Ce, La 578: Dy 600: Sm 648: Sm 780: Nd	β-Ca-phosphate	[1]
Nakhla	514:Al, REE	Chloroapatite	[2]
Y-000593 (nakhlite)	578: Dy 598: Sm 650: Sm	Apatite	[3]

Table 1: CL properties of three Martian meteorites.

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Micro-Raman spectroscopy and optical reflectance studies of coals with different rank

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Powerfull techniques for studying changes in the structure of organic matter during coalification and graphitisation processes include micro-Raman spectroscopy and optical reflectance.

Since coal is a heterogeneous rock with different maceral composition, the coalification studies should include the properties of each individualized component and not the average samples. Therefore, micro-Raman spectroscopy and optical reflectance analysis were performed on collotelinite and fusinite macerals from a set of coals with increasing rank.

The Raman analysis indicates the presence of bands at 1580 cm^{-1} (G), 1470 cm^{-1}, 1350 cm^{-1} (D1) and 1170 cm^{-1} on the first-order Raman spectrum on both macerals from the different coal samples. From table 1 several differences between both macerals can be observed, lower values of FWHM$_G$ and higher values of reflectance, v_G and D1/G were obtained on fusinite in all samples with the exception of sample 3153 (anthracite). With increasing reflectance a narrowing of the G band and its shift toward higher wavenumbers occur on both macerals. However the D1/G intensity area show a slight decrease on collotelinite (except for sample 3153) and a rather constant values on fusinite. The results show that within the same coal sample the Raman parameters and reflectance in collotelinite and fusinite are different and their evolution with increasing of coal rank is also different.

Table 1: Raman parameters and reflectance of collotelinite and fusinite macerals from a set of coals of increasing rank.

Sample	Collotelinite				Fusinite			
	Ro	v_G	FWHM$_G$	D1/G	Ro	v_G	FWHM$_G$	D1/G
3157	0.50	1591	59	2.1	5.15	1591	54	3.2
3158	0.63	1591	67	1.2	4.27	1594	53	3.7
3159	0.78	1591	57	1.8	4.51	1591	56	3.5
3155	0.90	1588	59	2.0	3.81	1592	48	3.4
3156	1.14	1589	54	1.9	4.28	1594	45	3.7
3152	1.41	1588	55	1.8	4.63	1596	48	2.9
3160	1.96	1591	46	1.7	5.05	1592	44	2.8
3153	4.28	1596	34	2.5	6.11	1594	42	3.3

v_G: G band wavenumber; FWHM$_G$: full width at half maximum of G band; D1/G: intensity area ratio; all are mean values; Ro: mean random reflectance.

Acknowledgements

Stable isotope fingerprinting of iron metabolism in higher plants

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The fractionation of stable iron isotopes by biological processes is currently a matter of intense debate. Our study is the first to show that higher plants fractionate stable iron isotopes during Fe acquisition and translocation in a significant and plant-specific manner [1].

To maintain an optimal iron supply plants have adopted two different strategies to acquire iron from the soil [2]. Strategy I plants reduce Fe(III) in the rhizosphere, as only Fe(II) can be transported across the plasma membrane of root cells. Strategy II plants acquire Fe(III) by complexation with phytosiderophores. In which form iron is translocated from roots to shoots is so far unclear [3].

Stable iron isotope compositions reflect these two uptake strategies when soils are Fe sufficient [1]. Reduction of Fe(III) in soils by strategy I plants results in the uptake of light iron compared to the available Fe in soils; complexation with siderophores by strategy II plants results in only minor fractionation. Furthermore, younger parts of strategy I plants get increasingly depleted in heavy isotopes from the first to the fourth leaf, while strategy II plants incorporate Fe of virtually uniform isotope composition throughout [1].

Here we report new results of changes in Fe isotopic compositions of strategy I (tomato, bean) and strategy II plants (oat) during growth in a nutrient solution environment under Fe-sufficient conditions. Older leaves of strategy I plants get increasingly enriched in heavy Fe isotopes whereas younger leaves become lighter while the plant grows ($\delta^{56}Fe =$ up to -3 $\pm$ 0.05 (2SD) ‰). In strategy II plants all parts of the plant incorporate similar isotope compositions during growth. These results now show that indeed younger leaves of strategy I plants receive a substantial proportion of their Fe from older leaves. Apparently differences in iron translocation mechanisms between strategy I and II plants exist. Inside the plant Fe is scavenged by complexing agents, e.g. nicotianamine in the cells or citrate in the xylem. Nicotianamine has the ability to bind ferrous and ferric iron. The current hypothesis is that strategy I plants change the Fe redox state during translocation. In contrast, Fe in strategy II plants remains in the ferric state but changes its ligands.

Under Fe deficiency plants mobilize Fe from phytoferritin in older leaves, which includes a reduction step. The challenge is now to assign Fe isotope labels to these redox changes during re-/translocation.

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Further evidence for a two stage magmatic underplating event in the Ivrea-Verbano Zone, Italy

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Magmatites of the continental crust are essentially formed by two tectono-magmatic processes: In the course of subduction and by the way of "magmatic underplating". While subduction processes can be studied at many different places world-wide, the process of "magmatic underplating" can only be studied directly in the Ivrea-Verbano Zone (IVZ) of the Southern Alps (Italy). So our understanding of this not less important mechanism of crustal growth is still unsatisfactory inasmuch as reliable age data providing tight time constraints on the duration of the underplating processes are still missing. One of the major open questions still is, for instance, whether magma formation and emplacement is a discrete or a continuous event. The IVZ is interpreted as being a slice of the South-Alpine lower crust intruded by mantle magmas. Rocks of this zone have been grouped in two major units, the voluminous composite Mafic Complex (=Mafic Formation) and the high-grade paragneiss Kinzigite Formation. For the main intrusive body of the Mafic Complex in the Val Sesia and Val Sessera sections an intrusion age of 288 ± 4 Ma is postulated [1]. This speaks in favour of a short, discrete main underplating event in the Lower Permian. In addition, the age data indicate that a significant thermal event affected the country rock of the Mafic Complex around 310 Ma, the significance of which is not yet clear. "Strati-graphically" this thermal event seems to be most prominent in the lower most parts of the crust. We have investigated the Campello Monti and Monte Capio area (Val Strona). Here the Mafic Complex forms a composite intrusion which only in parts can be paralleled with the main intrusive body in the Val Sesia. Especially an amphibole-garnet-bearing gabbro strongly resembles the amphibole-gabbro of the lower mafic complex in the Val Sessera [1]. From the former a zircon LA-MC-ICP-MS U-Pb intrusion age of 331.5 ± 3.8 Ma could be determined. This new age is the first unequivocal evidence that an older magmatic event occurred in the lower part of the IVZ crust in the Middle Carboniferous. This substantiates that the underplating event in the IVZ indeed was a long lasting process with a duration of ca. 50 Ma but comprising a number of discrete intrusive phases of only a few million years duration. The geodynamic implications of this new aspect in the evolution of the IVZ in the framework of the Variscan orogeny, mainly the onset of crustal thinning already in the Carboniferous, remain to be investigated.

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Silica polymerization. Rate constants at 23° to 80°C as a function of pH

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When monomeric silica concentration exceeds the solubility of amorphous silica monomeric silica reacts to form polymeric silica. It is generally agreed that the polymerization proceeds until the concentration of monomeric silica is equal to the solubility of amorphous silica. Much work has been done over the years to determine the rate of silica polymerization but to date there is no general agreement on rate laws. Rate orders of 1 to 8 and rate maximum between pH 6 to 9 have been reported. Part of the discrepancies is probably due to failures to recognize things like induction periods and failure to account for higher amorphous silica solubility at high pH values.

After the initial stages of silica polymerization, where silica is forming nuclei of critical size, the polymers have a tendency to maximize the number of siloxane bonds (Si-O-Si) and minimize the number uncondensed SiOH groups and they become spherical units. These polymers grow with addition of monomeric silica on their surfaces. At this stage of silica polymerization there is equilibrium between the silica polymers and monomeric silica in solution. As polymerization continues the polymers increase in size and the area, to which the monomers are added, is continuously changing affecting the polymerization rate. Silica polymerization stops when the polymers are so big that surface energy does not contribute much to the total energy of the polymers. Polymers of that size have similar solubility as amorphous silica.

In this contribution are presented the results of silica polymerization experiments in the pH range 5.66-9.18 at 23°, 2.48-8.50 at 58° and 2.18-8.75 at 80°C. Ionic strength was 0.11±0.02M in all cases. Rate of silica polymerization was monitored by analyzing concentration of molybdate active silica. Results indicate that the rate of silica polymerization is greatly affected by the pH value of the solution and there is no maximum in polymerization rates over the pH range of this study. The calculated rate constants increase with rising pH value over the whole pH range of the experiments at all experimental temperatures.

The sulphur isotopic evolution of late Neoarchean and early Paleoproterozoic seawater

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Despite its well accepted importance for reconstructing the redox evolution of Earth's ocean-atmosphere system, our knowledge of the abundance and isotopic composition of seawater sulphate decreases substantially with increasing time. This is most apparent for the Precambrian. In particular, the proposed rise in atmospheric oxygen abundance (Great Oxidation Event) around 2.3 Ga ago and an assumed parallel increase in the abundance of dissolved oceanic sulphate is not documented at all.

Here, we report abundances for sulphate sulphur as well as sulphur and oxygen isotopic compositions for the Neoarchean-Paleoproterozoic succession deposited on the Kaapvaal Craton between 2.65 and 1.92 Ga, i.e. the Transvaal Supergroup of eastern Transvaal and correlative units in the Griqualand West Subbasin.

Trace sulphate extracted from 16 carbonates of the Koegas, Duitschland, Mooidrai, Silverton and Lucknow formations gradually increase from less than 0.1 to 23.5mmol/kg. The respective sulphate sulphur isotopic composition varies between +4.6 and +34.6‰ with a distinct stratigraphic trend being discernible. The oxygen isotope values for the trace sulphate displays a range between +6.1 to +21.1‰.

Individual stratigraphic units are well constrained in their isotopic composition. Yet, the truly global significance of the isotope record needs to be verified with additional analyses. So far, respective host carbonates have provided a carbonate carbon isotopic composition that includes pertinent features considered characteristic for this time interval, such as the globally recorded ^{13}C maximum (the Lomagundi-Jatulian event).

Acknowledgements

Trace element and Ca isotope ratios in calcareous dinoflagellate cysts of *Thoracosphaera heimii*

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Dinoflagellates are important marine primary producers, which significantely contribute to the global carbon-cycle. They can form cysts, composed of organic-material, silicate or calcium carbonate, which are used as stratigraphic and paleoenvironmental indicators.

The export flux of calcareous dinoflagelate cysts is of particular importance in temperate to tropical waters and is dominated by the species *Thoracosphaera heimii*. Providing a significant calcium sink, their Ca isotope fractionation is an important factor for the Ca isotope ratios of the locally deposited carbonate oozes, but might also be important for defining the isotopic Ca budget of the ocean. In addition, *T. heimii* cysts provide the potential to record long-term changes in the ocean chemistry, because their first occurrence dates at the K/T boundary [1].

The $CaCO_3$ cysts of *T. heimii* might be particularly useful as proxy archive recording ocean surface conditions (e.g. temperature, pH) due to their formation at the deep chlorophyll maximum depth in the water column and the ease in which a monospecific assemblage can be isolated from sediments [2]. Furthermore, they are comparatively insensitive to dissolution.

The dominant calcareous dinoflagellate *T. heimii* was grown in lab cultures at varying temperatures ranging from 12 to 30 °C as described earlier [3]. Trace element to Ca and Ca isotope ratios were analysed on the $CaCO_3$ cysts, previously cleaned from organic components.

The Ca isotope fractionation for *T. heimii* cysts resembles previous calibrations of other marine calcifyers, including coccolithophores [4], foraminifers and corals [5], in respect to absolute fractionation and temperature sensitivity. In contrast, trace element to Ca ratios and their temperature dependence differ from trends observed for coccolithophores and planktonic foraminifera. These results will be discussed in terms of biomineralisation of *T. heimii* and potential use for paleoceanographic applications.

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Mechanisms of iron(III) binding to organic matter and its competitive effect on trace metals

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Organic complexation of iron(III) is important for the binding of trace metals in natural environments because of competition effects. We have investigated the binding mode of iron(III) in the presence of O horizon soil material and isolated fulvic acid by means of EXAFS spectroscopy. The spectra for the O horizon samples showed Fe-O/N interactions at 2.02(2) Å, second-shell Fe-C interactions at 3.00(4) Å, and a mean Fe-Fe distance at 3.37(3) Å (Gustafsson *et al.*, 2007). This showed that the major part of the organically complexed iron(III) was hydrolyzed, and comparisons with literature data revealed that iron(III) had formed a mixture of di- and trimeric complexes with soil organic matter. The results were used to constrain a model for organic complexation, the Stockholm Humic Model. Observed competition effects on Cd^{2+}, Cu^{2+}, Ni^{2+} and VO^{2+} were well described with a single dimeric iron(III) complex in the model. In another set of experiments iron(III) was equilibrated with isolated fulvic acid at different initial pH:s, and the mixtures were analyzed with EXAFS spectroscopy after different time periods. These spectra lacked the Fe--Fe distance at 3.37 Å, instead Fe formed a monomeric iron(III) complex with FA or was reduced to Fe(II) after prolonged equilibration times. Our results indicate that the iron(III) binding modes to organic matter need not be identical in soils and aquatic environments. In soil suspensions any added iron(III) is quickly polymerized, whereas in solutions significant amounts of iron(III) complexes may remain as monomeric organic complexes. This shows that much remains to be done before the aquatic geochemistry of iron(III) is fully understood.

Reference

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Identifying processes and rates of incipient chemical weathering using Pb and U isotopes

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This study focused on the role of incipient chemical weathering on combined U and Pb isotope systematics. Understanding the effect of incipient weathering is particularly relevant for interpreting the marine Pb isotope record during glacial-interglacial transitions. Here, we investigate whether the preferential release of radiogenic Pb, displaced through alpha recoil, could explain Pb isotope variations during the recent deglaciation. Soil samples from a granitic chronosequence at the forefield of the Damma glacier were sampled for an experimental study of chemical weathering. A sequential leaching technique was employed on the <1mm grain size fraction (0.05M, 0.1M HBr; 0.05M, 0.6M HCl; leaching each fraction for 24 hours in a shaker) and the residue dissolved by pressure digestion. In order to distinguish the effects of preferential dissolution of U- and Th-rich minerals (Harlavan *et al.*, 1998) and release of alpha-recoiled Pb, we measured both the Pb isotope compositions and $\delta^{234}U$ (expressed as the permil $^{234}U/^{238}U$ variation from secular equilibrium). Most strikingly, even the moraine samples with the youngest depositional age (<10 years) are depleted in ^{234}U ($\delta^{234}U = -26‰$) and the most depleted $\delta^{234}U$ is found for moraine material that was exposed to chemical weathering for several decades ($\delta^{234}U$ as low as -43‰). The negative $\delta^{234}U$ in the leachates suggests that the soil material has already been affected by fast chemical weathering without any indication of preferential release of ^{234}U during leaching. Similarly, the various radiogenic Pb isotope compositions ($^{206}Pb/^{204}Pb$ in particular) do not show any sign for the presence of α-recoiled Pb. The Pb isotopic trends in all leached moraine samples suggest relatively congruent release of natural bulk Pb from the finest sediment fraction during the first leaching steps (although a slight offset by anthropogenic Pb contributions might be present in the first leachates). Continued leaching leads to systematic shifts towards very radiogenic $^{206,207,208}Pb/^{204}Pb$ only in the youngest samples, whereas older soil samples do not display this trend. While $^{206,207}Pb/^{204}Pb$ in the residue is lower than that of leach fraction #4 (0.6M HCl), the residual $^{208}Pb/^{204}Pb$ is systematically higher than the extracted phase. We attribute this feature to variable resistance of the U- and Th-rich minerals to weathering. Overall the U- and Pb-isotopic trends observed in this study indicate that, for the Damma glacier lithology, the depletion of U- and Th-rich labile accessory phases (such as apatite) occurs within tens- to a maximum of hundreds of years, as opposed to much longer timescales suggested in earlier studies.

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Dissolution of magnetite in hydrothermal solutions: Kinetics and speciation by *in situ* X-ray absorption spectroscopy

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In the research program on mineral sequestration of CO_2, time-resolved studies dedicated to fluid-rock interactions are essential. Magnetite ($Fe^{II}Fe^{III}_2)O_4$ is an accessory host solid phase (the most reactive host candidates are basic and ultra-basic rocks), but is likely to release critical amounts of dissolved iron in the fluid, iron which is a reactant for the carbonation of carbon dioxide. Furthermore, magnetite may play a major role in the redox control of the system. For those reasons, we studied the dissolution of magnetite in hydrothermal conditions, as a function of pH, temperature and the nature of ligands in presence (the roles of sulfate and chloride ligands were quantitatively compared).

Our methodology is based on *in situ* x-ray absorption spectroscopy (XAS) on synchrotron sources. For that purpose, we use an high-pressure/high-temperature cell (Testemale *et al.*) that allows, in the same run, the determination of iron molality in the fluid in contact with a monocrystal of magnetite, the kinetics of this dissolution, and the measurement of X-ray absorption spectra at the iron K-edge (see Figure 1). The latter is a strong point of this method: the speciation and oxidation state of dissolved iron can be inferred from these x-ray absorption spectra.

We will present a kinetics model for the dissolution of magnetite, in the conditions investigated (300 bar, [30-300°C]), to be compared with literature data. In particular, the role of iron speciation and the stoichiometric nature of the dissolution will be discussed.

Figure 1: Total iron molality (Fe^{II} and Fe^{III}), as a function of time, in a 2.5M sulfuric acid solution. For each point, we acquired a XAS spectrum from which the speciation is determined.
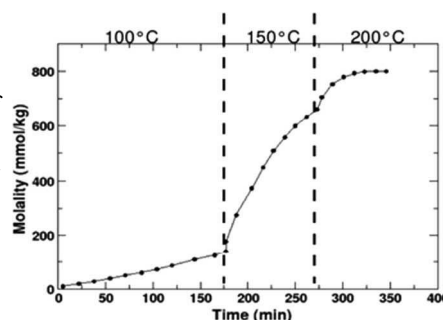
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Apatite- and K feldspar-hosted primary carbonatite melt inclusions from mantle xenoliths, Hungary

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Samples

We studied metasomatic mantle xenoliths, consisting of clinopyroxene, apatite, K feldspar and phlogopite, were found in lamprophyre dikes in central Hungary. A large number of multiphase primary carbonatite melt inclusions (CMI) were observed in apatite and K feldspar, but clinopyroxene and phlogopite are barren. Average PM normalized REE distribution of apatite and K feldspar hosted CMI (n=60 and n=20, respectively) are shown on Fig. 1. Both CMI in apatite (Ap) and K feldspar (Kfs) are extremely enriched in LREEs relative to HREEs analyzed by LA-ICP-MS.
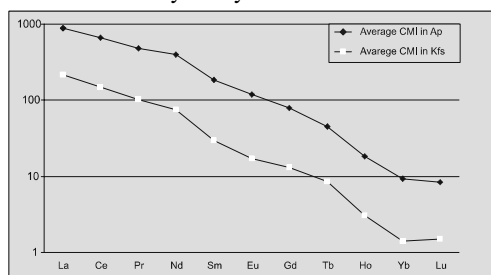

Figure 1: PM normalized REE patterns.

Discussion

It is a characteristic geochemical feature that CMI in Kfs contain small amount of P and that in Ap do small amount of K. The REE distribution of CMI in both host minerals show similar pattern (Fig. 1), suggesting common origin of their melts. It is also supported by some unique CMI hosted in Ap having trace element composition and pattern similar to CMI of K feldspar. All of these indicate that there was a liquid-liquid separation between a P-bearing carbonatite melt and a carbonate-bearing silicate melt before crystallization of the host minerals. It seems that the liquid-liquid separation was caused by dramatic compositional change in the continuously migrating "initial" carbonatite melt. This change was linked with an open-system metasomatic interaction between the "initial" melt and the peridotite mantle.

Conclusion

The studied xenoliths were formed by metasomatic interaction between the peridotite mantle and the P-bearing, Mg-calcitic "initial" carbonatite melt.

Fluid composition, density and viscosity changes along terrestrial Pressure-Temperature paths associated with particular tectonic processes

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Physical properties determine how buoyant fluids rise (density) and how fast they flow (viscosity). Such physical properties will also depend on fluid composition, especially where mineral solubility is high. We have modeled the thermal and chemical behavior of dehydration fluids with dissolved constituents generated in and above subduction zones, and also along burial and exhumation paths in the crust. Silica solubility has been used as an example (e.g., Gerya et al. 2005). SiO_2–H_2O fluid viscosities at quartz-saturation have been modeled following Audétat & Keppler (2004). Silicate-bearing fluid densities have not yet been measured, so in the interim, we have modeled SiO_2–H_2O fluid densities at quartz-saturation. We assumed an ideal mixture and combined solubility data with properties of the end-member liquids. The results show that fluid-rock interactions are likely to follow distinct patterns along different PT paths. For example, buoyant fluid flow into the overlying hot mantle wedge is up T (while down P) and follows a dissolution path, whereby fluids may create permeability, facilitating higher fluxes. Fluids flowing along the slab-mantle interface move to lower T and P and precipitate dissolved matter, which acts to decrease porosity and probably permeability and reduce flow rates in that direction. Our analysis reveals that subtle differences in fluid PT ascent paths, strongly influence both solubility and fluid density-viscosity evolution along paths and thus also the efficiency and rate of mass transport. Low-viscosity and low-density fluids have the greatest chance of moving at higher velocities. With increases in density, solute concentration increases, buoyancy decreases and viscosity increases. Increased solubility of mineral in fluid thus decreases ease of ascent, but tends to work in the opposite PT direction. So fluids related to rock burial become increasingly dense and more viscose, and thus less mobile. In contrast, rising fluids tend increase their buoyancy and decrease their viscosity but because solute concentrations also decrease, fluid ascent can become restricted by precipitation.

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