Topographic and hydrologic controls of spring water travel times and plagioclase weathering rates in solid rocks

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Two sets of springs, one associated with watersheds on average smaller than 10 ha (short hydraulic circuits) and discharging 10 L/min and the other linked to watersheds on average larger than 50 ha (longer circuits) and discharging 24 L/min, were selected for this weathering study in North Portugal. Using hydrograph analysis methods it could be calculated for the first set (30 springs from the Sordo river basin, characterized geologically by granites and schists), hydraulic conductivities $K = 2 \times 10^{-6}$ m/s and drainable porosities $n_e = 5 \times 10^{-2}$, which were found to be 4 and 5 times larger than the $K$ and $n_e$ values of the second set (14 springs from amphibolites of the Morais massif). Subsequently to the estimation of $K$ and $n_e$, hydrologic travel times ($t$) were determined by a numerical (finite differences) method assuming the system to be at steady-state and the transport of solutes to be advective. In the Sordo basin $t = 3.7$ yr whereas in the Morais massif $t = 13.6$ yr. The conclusion was: the longer paths in Morais conducted amphibolite water deeper into the fractured massif, where $K$ and $n_e$ were smaller, and as result longer times were necessary to complete the corresponding hydraulic circuits. The hydrograph analysis methods also produced numbers for the surface area of plagioclase ($A_{Pl}$, m$^2$) reacting with aquifer water in unit time (1 yr), while concentrations of dissolved plagioclase at spring site ($[Pl]$, mol/L) were determined by the SiB Algorithm [1]. Finally, plagioclase weathering rates ($W_{Pl}$, mol/(m$^2$.s)) were calculated by the formula: $W_{Pl} = [Pl]/t \times V/A_{Pl}$, where $V$ is the volume of groundwater with steady-state concentration $[Pl]$ that discharges at the spring site in unit time. The weathering rates span three orders of magnitude on a secular basis (Fig. 1). The drop in the rates follows a power function described by $W_{Pl} = 1.5 \times 10^{-13} \times t^{-1.37}$, suggesting control by transport-limited reaction. A similar power function was used by [2] to describe silicate weathering.

![Figure 1: Relation between weathering rates and time.](image)

References

Solar nebular fractionation of refractory elements Y and Ho

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The geochemical twins Y and Ho are both trace elements in chondrites and most of their components. Both are highly refractory and condense at high temperatures. No or only little fractionation between Y and Ho is expected in igneous or metamorphic processes. This makes the Y/Ho-ratio a suitable tracer for chemical heterogeneity in solar nebula reservoirs. We report Y/Ho-ratios of CAIs, chondrules and bulk chondrites.

Bulk samples were fused by means of a containerless technique to small (~2 mm) sheres, which were embedded into resin for EPMA and LA-ICPMS.

Fusion in combination with LA-ICPMS allows determination of Y/Ho-ratio with a relative error <0.5% (2σ). CCs (C11, CM2, CV3, CK4) have uniform Y/Ho = 25.94±0.08 (2σ). LL-, L-, H- and E-chondrites have increasingly elevated Y/Ho-ratios (see figure). CCs have a Y/Ho-ratio that is suggested to represent the ratio of the solar system. Elevated Y/Ho-ratios of OCs and ECs are interpreted as result of loss of a fractional condensate with subsolar Y/Ho. This component may have been similar to CAIs with Group-II REE patterns, which have subsolar Y/Ho. Removal of fractional condensates may also be responsible for elevated Re/Os in ECs relative to CCs. Data of terrestrial rocks (herzolite, basalt) show that partial melting fractionates Y and Ho. The bulk Earth is suggested to have a solar Y/Ho-ratio, which excludes ECs as parental material to the Earth.
Atypical SHRIMP II REE data in zircons: A positive Eu anomaly

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Distribution of REE depends on some factors:
- temperature and pressure of melt
- interaction with enclosing strata
- sequence of crystallization
- crystalchemistry of the host mineral

Enrichment in HREE as well as depletion in LREE with contrast negative Eu and positive Ce anomalies are typical for zircon structure in common case (fig.1a).

Unusual REE distribution patterns were recorded in zircons at recent investigations. They show a positive Eu anomaly with portion of LREE enrichment (fig.1b).

Figure 1: Chondrite normalised REE patterns: a. typical for zircon; b. atypical REE distribution.

Such REE distribution patterns were observed in the following cases: 1) in zircons from low crustal eclogitic xenoliths from an eruption pipe at Elovy Island (White sea), 2) in zircons from Kalaknda massif granulites (Kola peninsula), 3) in zircons from Antarctic alkaline pegmatites. The U-Pb data show the discordant ages of these zircons as well as high magnitude Th/U ratio variation. Thus, the effects of REE pattern deviations are connected with metasomatic and metamorphic processes. These influences have an effect in Eu and LREE increasing. Hence, these REE patterns could be considered as secondary processes affecting.

References

Laser ablation study of trace elements in chromite: Thetford Mines ophiolite chromitite ores

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This study aims to identify compositional contrasts between chromitite ores from the Thetford Mines Ophiolite (TMO), Canadian Appalachians, which contains more than 30 chromitite deposits grouped into 3 principal types, and to better understand the mechanisms of their formation.

The 3 types of chromitite are: 1) podiform chromitite found in mantle peridotite, 2) stratiform chromitite from rocks formed at the base of the crust, and 3) intracrustal discordant chromitite close to, or in crustal pyroxenites. Fractional crystallization, magma mixing, country rock assimilation, melt-rock reaction, or a combination of these processes have been proposed as important in chromitite formation. There is also a relationship between chromitite deposits and platinum-group elements (PGE) deposits.

Chromitite deposits from ultramafic-mafic layered intrusions are frequently associated with high concentrations of PPGE (Rh, Pd, Pt). Ophiolite chromitite deposits contain intermediate levels of IPGE (Os, Ir, Ru) and laser ablation analysis of PGE in chromite allows us to verify that these elements are not incorporated in chromite structure (solid solution) with the exception of Ru with concentrations from 38 to 134 (± 20) ng/g. The high PGE concentrations of ophiolite chromitites are principally related to the observed platinum-group minerals (laurite – erlichmanite series) included in chromite grains.

Our trace element analysis include Mn, Ni, Co which appear to have reequilibrated with the olivine of host dunite rocks as have Fe and Mg, therefore it is difficult to determine whether fractional crystallization or contamination (magma mixing or host rock assimilation), processes trigger chromite precipitation. On the other hand, our preliminary analysis of Ti, V, Ga and Zn, which are less sensitive to reequilibration with olivine, show an evolutionary trend compatible with fractional crystallization (negative correlation with Cr#).
Equilibration of the Earth-Moon system following the giant impact

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The energy released in the Moon-forming giant impact is sufficient to melt and partially vaporize both the Earth and the impactor. The timescale to eliminate this heat by radiation is ~10^3 years. Hence, the Earth and protolunar disk are expected to be molten and enveloped by a convecting silicate vapor atmosphere for the first thousand years following the giant impact.

To explain the striking similarity of the oxygen isotopic composition of the Earth and Moon [1], we have previously proposed that the terrestrial magma ocean and the protolunar magma disk underwent equilibration in the aftermath of the giant impact through exchange with the common silicate vapor atmosphere [2]. Recent support for this idea comes from precise measurements of silicon isotopes that reveal the Moon to have a composition similar to the silicate Earth, a property not shared with Mars, Vesta, and chondrites [3].

Due to the liquid/vapor partitioning of the elements [4], such a model does not imply a chemical composition for the Moon that is identical with the silicate Earth. The ability of the vapor to exchange between the Earth and lunar disk, to undergo more vigorous turbulent motions than the liquid, and to preferentially escape in a hydrodynamic outflow will effect the chemical composition of the resulting Moon. We are presently undergoing an investigation of the consequences of the equilibration hypothesis to explore the extent to which this scenario can explain the similarities and differences in the Earth-Moon system.

References

Precipitation and phase transformations involving ferric arsenate, scorodite and arsenical ferrrihydrite

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Arsenic is a common contaminant in the effluents resulting from gold and base-metal processing and related extractive metallurgy operations. Conventional industrial practice of arsenic control and stabilization involves coprecipitation with ferric iron in a high-density sludge system as a ferric arsenate having molar Fe/As ratios of about 4 and greater. Ferric arsenate characterized by two broad humps on powder X-ray diffraction patterns has been reported from mine tailings, acid mine drainage precipitates, microbial mats at a geothermal spring and a sea-floor hydrothermal vent, and often referred to as the “amorphous” scorodite. Solubility studies have produced controversial results, with low to high solubility values which appear to have stemmed, in part, from the complexity of the ferric arsenate compounds that was not resolved by the characterization techniques employed. In order to provide insights into the nature of ferric arsenate and its relations to scorodite and ferrrihydrite, a series of synthesis experiments were carried out at 70°C and pH values ranging from 1 to 4.5. The precipitates were characterized by high-resolution transmission electron microscopy, X-ray diffraction and X-ray absorption fine structure spectroscopy techniques. Experimental results including the nature of ferric arsenate and arsenical ferrrihydrites having a wide range of arsenic concentrations, phase transformations and crystallization kinetics will be presented.
Hf-W chronometry of chondrites
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The total Fe content of chondritic meteorites is variable, reflecting separation of metallic iron in the early solar system. Such metal-silicate fractionations should be accompanied by fractionations of Hf from W and, hence, their timing can be studied using 182Hf-182W chronometry. Here we present Hf-W and bulk chemical data of large, homogenized samples for various groups of chondrites with the ultimate goal to date the metal-silicate fractionation in the early solar nebula. Both, Hf/W and 182W/184W ratios increase in the order of H-L-LL chondrites, as expected from the abundance of metal in these chondrites. However, there are substantial variations in the Hf/W ratios within the H and LL chondrite groups, which may indicate W mobility during parent body processes. These currently hamper precise dating of the Hf-W fractionation among the chondrites. All LL chondrites studied here (including type 3) plot below the CAI isochron [1], suggesting that the Hf-W fractionation, i.e., metal silicate separation post-dated formation of CAIs by a few Myrs. More data, particularly for the most primitive chondrites are needed to confirm this observation. An important aspect of our new data is that H chondrites, on average, have lower Hf/W ratios than carbonaceous chondrites, whereas L chondrites have Hf/W ratios indistinguishable from carbonaceous chondrites [2,3]. This is unexpected given the fact that H chondrites have Fe/Mg ratios similar to those of CI chondrites, but L chondrites have lower Fe/Mg ratios. This and the relatively low W contents in metals from type 3 ordinary chondrites [4,5] could indicate that a significant part of the W did not condense as metal. If this is true, conditions in the chondrite formation region must have been rather oxidizing.

References

Lead origin and fate in soils:
Geochemical records in buried soils over the past 3500 years
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Methods
The effect of climate fluctuations and anthropogenic impact on lead origin and fate in Chestnut soils (Low Volga region, Russia) over the past three and a half millennia has been investigated. We compared the morphology, organic matter, soluble soil, gypsum, carbonates, total lead content and Pb isotope ratios in the profiles of modern soils and soils buried under the burial mounds, dated using archaeological methods. Buried soils form a chronological sequence from XVI-XV centuries BC till nowadays.

Results and discussion
Comparison of buried soils and their modern analogues demonstrated that during the past 3500 years the cyclic reversible changes of climate took place in this region. Drought epoch had started 4500 years ago with maximum between 2000 BC and 3000 BC. The most moist climate conditions were found in XII-XIV cent.

We observed an increase of total lead concentration in upper soil horizon along soil chronological sequence probably reflecting a growing anthropogenic input of lead. However the difference in total lead content and isotope ratios between modern and buried soils is statistically significant only for soils buried before the middle ages. Lead isotope ratios in upper horizons of modern soils (207Pb/206Pb and 208Pb/206Pb) fit to European Standard Pollution Line and Russian-GDR gasoline line (Haack et al., 2003), reflecting the influence of airborne Pb, deposited from a continent-wide mixing system or local sources of Pb-gasoline.

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Evolution of Manzanillo batholith Complex: Structural data, thermobarometry and geochronology

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The Manzanillo batholith Complex (MBC) occurring along the south-western shores of Mexico is related to the Latest-Cretaceous convergence between the Farallon and North-America plates. The MBC is composed of metallocumious granodiorite and granite, with a gabbro-diorite core, which intruded into the Cretaceous volcano-sedimentary arc sequences of the Guerrero terrane.

Structural, geochemical as well as SHRIMP U/Pb zircon geochronology data suggest that the MBC is a composite batholith and it was formed by several magmatic bodies. They were emplaced at different depths and different times ranging from 74 to 62 Ma: five Granite Complexes (GCs), a Granodiorite Complex (GdC) and a Gabbro Complex (GbC).

i) The main rock-type is a medium grain size granite associated with minor granodiorite and porphyry dikes (GrCs). They are typically calc-alkaline and relatively K-enriched. The oldest granitic complex was emplaced 74 Ma ago and the depth emplacement ranging between 6 and 12 km.

ii) Grain coarse Granodiorite Complex (GdC) shows a discrete internal foliation and it is compositionally homogeneous with LILE enrichment, fractionated LREE with a distinct negative Nb anomaly and flat HREE patterns. It apparently was emplaced at shallow crustal level (< 2.8 kbar) and at 62 Ma ago.

iii) Massive gabbros and minor isolated small cumulitic bodies (associated with brown Am replacing Cpx) and diorite rocks constitute the Gabbro Complex (GbC), which occurs essentially in the central part of the MBC. GbC magmatic textures are preserved apparently in place, but locally subsolids reactions and plastic deformation are observed. Near the contact between the GdC and GbC the gabbros are affected by melt infiltrations with a growth of Bt, Qtz, Kfs. Pl presents rounded and corroded rims. GbC is slightly older (68 Ma) and deeper than GdC.

On the basis of field, geochemical and geochronological data we argue that GbC intruded at about 15 km depth and successively was affected by subsolids recrystalization and deformation before or during fast uplift. Chemical composition support a fluid slab-related contamination and a tectonic emplacement at shallow crustal levels for these bodies.

High primary productivity in stromatolitic phosphorites from the Paleoproterozoic Aravalli Supergroup

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Paleoproterozoic biogeochemical cycles were fundamentally changed by glaciations and the accumulation of atmospheric oxygen. Higher levels of seawater sulfate and atmospheric oxygen have been inferred from Paleoproterozoic interglacial sedimentary sulfides with sulfur isotope compositions characterized by large ranges of δ34S values and the absence of mass-independent fractionation (Papineau et al., 2004). Carbon isotope excursions in Paleoproterozoic interglacial carbonates from the Transvaal Supergroup and in post-glacial carbonates on most continents indicate high burial rates of organic carbon and suggest a significant production of atmospheric oxygen (Bekker et al., 2004). Because atmospheric oxygen is primarily produced by oxygenic photosynthesis, these observations suggest enhanced primary productivity during the Paleoproterozoic. This was perhaps modulated by higher nutrient availability in seawater, such as phosphate, which could have resulted from post-glacial greenhouse conditions and accelerated weathering of continental crust.

We present new carbon isotope data from dolomite, carbonate fluorapatite and organic matter in stromatolitic phosphorites from the Paleoproterozoic Jhamarkotra Formation of the Aravalli Supergroup, India. Carbonate fluorapatite from columnar stromatolites is systematically depleted in 13C (-1.8 to -0.2‰) compared to intercolumnar dolomite (-0.3 to +0.6‰). These results suggest late diagenetic substitution in carbonate fluorapatite by HCO3 from the oxidation of organic matter. Total organic carbon extracted from these two phases overlaps in ranges of abundance and δ13C values, but are characterised by unusually heavy δ13C values up to -15‰. These carbon isotope data may reflect high levels of primary productivity during phosphorite deposition in the Jhamarkotra embayment. No carbon isotope excursion was found in stratigraphically lower and higher dolomites in the embayment, but excursions up to +5‰ exist in contemporary carbonates from nearby localities. Ongoing work with Re and Os isotopes could provide better age constraints for this unique phosphate deposit and relate it to other events of that time. In the context of Paleoproterozoic biogeochemical evolution, these phosphorites appear to record high biological primary productivity associated with post-glacial climate change.
Origin and evolution of ultrapotassic plutonic rocks (Durbachite series, Třebíč Massif, Czech Republic): An experimental approach

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To address the question of the origin of K-rich magmatism at the end of major orogenic episodes, an experimental study was conducted to constrain the crystallization conditions of mafic durbachite from the Třebíč Massif in the Bohemian Massif, Czech Republic. Durbachites are coarse-grained, porphyric plutonic rocks, typically containing large phenocrysts of K-feldspar, with high amounts of biotite, plus plagioclase, amphibole, augite and orthopyroxene. The durbachite series are abnormally K- and Mg-rich volcanic rocks and evolve from mafic to felsic end-members (SiO2=52-70 wt.%, K2O=7.3-5.5 wt.%, MgO=10-2.5 wt.%).

Crystallization experiments were performed in internally heated argon pressure vessels at 200 MPa, 900-1100°C, log fO2=NNO and NNO+3.6, and various water activities (XH2O of the coexisting fluid=0.3 to 1), using the most mafic natural durbachite as starting material. At 1100°C, only olivine crystallized (close to liquidus for XH2O=1), whereas olivine + biotite + augite crystallized at 1000°C. At 900°C, only biotite and augite (+apatite, zircon and magnetite) are stable phases in the investigated range of XH2O and fO2. K-feldspar, plagioclase, amphibole and opx are absent in all experimental products even at subsolidus conditions (~900°C and low XH2O). Thus, the natural mineral assemblage was not reproduced for the investigated range of T, fO2 and XH2O. Only biotite (Ti-rich: TiO2=3-5 wt.%, mg#=75-80) and augite (Wo44En42), present in natural sample, could be reproduced.

Our results indicate that the mineral assemblage of the mafic durbachite may not be the product of the crystallization of a melt with the investigated bulk composition at 200 MPa. If we consider that partial melting of enriched, heterogeneous subcontinental lithospheric mantle beneath the Variscan Orogen lead to the formation of the mafic durbachite (Holub, 1997; Gerdes et al., 2000), the observed mineral assemblage may indicate that (1) crystallization occurred at pressures or volatile activities significantly different from those investigated in this study (200 MPa, XH2O in the range 0.3 to 1) and/or that (2) incongruent reactions involving olivine, biotite and augite as reactants occurred at hypersolidus and subsolidus conditions. This hypothesis is supported by the presence of scattered clots of fine-grained actinolite mantled by biotite (“pilite”) that may be interpreted as pseudomorphs of olivine (Holub, 1997) and by the presence of augite as relics in amphibole. Another explanation is that the investigated mafic sample is not an end-member composition but a hybrid composition, contaminated by crustal material.


Interaction of copper with humic-coated gibbsite

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Both humic substances and mineral oxides exert important effects on chemical speciation and the transport of nutrients and contaminants in soils and sediments. Although most of the studies regarding chemical speciation in natural systems have been developed for individual reactive surfaces (mineral oxides, humic substances, clays), a better understanding on the subject could be achieved with mixtures of these components. The aim of this study was to compare the copper adsorption on gibbsite and HA-coated gibbsite.

First, the interaction of copper with the single systems humic acid (HA) and gibbsite was studied at different HA concentrations and pH. In order to explain the experimental results, the NICA-Donnan and the CD-MUSIC models were applied for Cu-HA and Cu-Gibbsite interaction, respectively.

The gibbsite was covered with different HA concentrations to study the copper interaction in a system that resemble more to the reactive surfaces present in natural systems. The adsorption of copper on the HA-gibbsite was higher than the adsorption on the single systems individually at the different pH values studied. This result was interpreted in a linear additivity model basis. The copper adsorption on the HA-coated gibbsite was also compared with a system consisting of HA, gibbsite and copper simultaneously added into the reaction vessel.
Mineralogical, geochemical, and microbial characteristics of marine sediments at Tempelfjorden Fjords, Svalvard, Norway

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Svalvard fjords, affected by turbid overflow emanating from outlet glaciers, are modern analogues for Quaternary deglacial settings. To better understand the response of the discharge of glacial meltwater including suspended sediments to the mineralogy, geochemistry, and microbial community, we sampled the subsurface sediments at 8 stations along the axis of Tempelfjorden fjords. The sediment samples were obtained using a gravity core at 1 station and a giant box core at 7 stations. The sediment samples were used for geochemical and mineralogical characterizations as well as for microbial community by genomic analysis. Iron-oxidizing and -reducing bacteria were enriched from the marine sediments at 8°C and the development of bacterial and archaeal structures in the sediments of fjords was examined using cloning and denaturing gradient gel electrophoresis analysis of rRNA gene. The water mass and marine sediments are influenced by the runoff from the glaciers at the fjord head in Tempelfjorden. X-ray diffraction analysis of the sand and silt fraction of the sediments revealed the predominance of quartz, mica, calcite, and dolomite with lesser amounts of feldspars and chlorite. Their clay mineralogy was dominated with illite, kaolinite, chlorite, and dolomite with lesser amounts of quartz, feldspar, and iron oxides. Iron-oxidizing and -reducing bacteria enriched from the marine sediments at 8°C and 25°C showed active Fe(II) oxidation and Fe(III) reduction. Iron-reducing bacteria enriched from the sediments were formed nm-sized magnetite at both 8°C and 25°C using lactate as an electron donor and a ferric iron oxide, akaganeite, as an electron acceptor. Dynamic bacterial community succession was observed at 8 stations. Although only one type of archaeal community profile was observed, archaeal community was quite distinct in the sediments and affected by deglaciation compared to control sediments. This confirms previous study that arctic sediment microorganisms participate in biogeochemical cycles remain in active at low temperatures.

Developing extraction method for mercury analysis in soils with different mineral composition

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The toxicity of elements depends not only on their total concentrations but also on their chemical forms. In real environment where mercury was considered as contaminant, we often experience difficulty in measuring mobility of mercury from constituents soils. The final goal of this project is speciation of mercury in contaminated soils and sediments. Preliminary tests for reference materials were performed to find out simple and more efficiency method to extract mercury. The reference materials with different mineral composition were selected and used. One is composed of mostly with Al-silicate minerals and another is mostly composed with calcite and ferrosilite. Same extraction method was applied to reference material of two types. The extraction efficiency for three methods was compared with certified values of reference material. The two extraction methods of three were acid digestion with aqua regia and mixed acid. The other extracted with mixture solution methanol and HCl using microwave at 40W and 80W for 20min respectively. The most high efficiency of sample including Al-silicate mineral was microwave method using methanol and HCl, while the calcite-based sample was observed that the aqua regia extraction method is good than the others. But this sample wasn’t detected with microwave method. The developing extraction method of the microwave using methanol and HCl will be possible to analysis of mercury more easily and rapidly. Also this can be applied to mercury speciation analysis in soils and sediments.
Geochemistry of basalt from the Eastern Woodlark Basin: Its implications for the mantle heterogeneity

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A section of the active spreading center in the eastern Woodlark Basin (EWLB) is subducting beneath the New Georgia Group, a volcanic arc. Basalt from the axis of EWLB were analyzed to investigate the processes in the region where ridge subduction and reversal in subduction polarity occurred in the past. They are similar to N-MORB in their major oxides, but are more depleted in incompatible elements. Incompatible element ratios such as Zr/Y and La/Sm show a large variation, which may be explained by mantle heterogeneity where an N-MORB source became mixed with or coexists with a different, mantle source that was depleted at an earlier time (Fig. 1a). The negative correlation between Ba/La and Zr/Y ratios indicates that the prior depleted end member is more enriched in the subduction component than the N-MORB mantle source and therefore may have originated from a subduction environment (Fig. 1b). The source of the subduction component remains to be explored by further studies.

![Figure 1](image1)

**Assessment of phosphorus and PAHs accumulation in the Suyoung river area in Busan, South Korea**

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**Method**

Sediment samples (0-50 cm in depth) were collected from the Suyoung river and the Hoedong drinking water reservoir area in Busan, South Korea to assess the accumulation of phosphorus and PAHs. Phosphorus was analyzed by an ICP-ES and a Spectrophotometer, and PAHs were analyzed using a GC/MSD. The phosphorus results are shown in the table below.

**Table 1. Phosphorus contents in the river- sediments.**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Adsorbed</th>
<th>Carbonate</th>
<th>Occluded in Fe-oxide</th>
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**Discussion and Results**

Most of the inorganic phosphorus was present being adsorbed onto the sediments and its concentration pattern was very similar to that of PAHs indicating the presence of phosphorus and PAHs were influenced by the geological characteristics of the area.

Concerning the source of PAHs, the upper part of Suyoung river may be influenced by pyrolytic inputs, where the middle or down part may be influenced by petroleum inputs, which can be the vehicle emission from fossil fuel combustion.

**References**


Geochemical and isotopic investigations of surface waters in Chuncheon, Korea

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The Han River is the largest river in South Korea in terms of the size of watershed and water discharge, and consists of two major tributaries: the North Han and South Han Rivers (NHR and SHR). The Soyang River (SR) is one of the major tributaries of the NHR, and joins the NHR at the Euiam Lake. In order to investigate geochemical and isotopic characteristics of river waters affected by a medium-sized city, Chuncheon, we have collected a total of 109 surface water samples from the NHR, the SR and the Euiam Lake. Of these surface waters, the SR is directly influenced by the city of Chuncheon, and it is characterized by much higher concentration of dissolved ions in the lower reaches relative to the NHR the Euiam Lake waters. Especially, it is observed that the concentration of dissolved ions of the SR is the highest in summer. Compared to the SR, the NHR is much lower in concentrations of dissolved solutes, indicating little contamination by anthropogenic sources. The Euiam Lake is located at the confluence point of both rivers, thus this lake waters plot between chemical compositions of both rivers indicating a mixing relation. On a plot of oxygen and hydrogen isotopic compositions, all water samples plot in a similar range near the local meteoric water line (LMWL) of Park et al. (2006), and this indicates all surface waters originate from similar sources of meteoric origin. Most samples are enriched in oxygen isotopic compositions, and thus slightly deviate from the LMWL, implying slight evaporation from reservoir surfaces.

Diel biogeochemistry of the Rio Agrio, Argentina

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Rio Agrio in Argentina is a geogenically acidic stream that derives its low-pH waters from springs on the flanks of the active Copahue Volcano. These springs are fed partially by off-gassing (SO2, HCl, HF) of the magma-chamber beneath the volcano. This study reports the results of three diel (24-h) water samplings in three different pH regimes (3.2, 4.4 and 6.3) along the river which is acidic for ~40km. Changes in the concentration and speciation of Fe dominated the diel chemical changes at all three sites. At the two lower pH sites, dissolved Fe(III) concentrations decreased during the day and increased at night, while dissolved Fe(II) showed the inverse temporal pattern. These cycles are explained by Fe(III) photoreduction, as well as a diel, temperature-dependent change in the rate of precipitation of hydrous ferric oxide (HFO). A correlation was observed between Fe(III) and As at the pH 3.2 site, most likely due to co-precipitation of As with HFO. At the downstream (pH 6.3) location, Fe(II) concentrations increased at night, as did concentrations of rare earth elements. Photoreduction does not appear to be an important process in this reach, although it may be indirectly responsible for the observed diel cycle of Fe(II) due to advection of photochemically produced Fe(II) from acidic upstream waters. These results are very similar to diel trends recently obtained from mining-impacted streams receiving acid rock drainage (Parker et al., 2007). The results help form a link between geochemistry and microbiology in acidic riverine ecosystems. For example, Fe(III) photoreduction produces chemical potential energy (in the form of metastable Fe2+) that helps support the bacterial community in this unique extreme environment.

References

Vertical tectonics in the Neoarchean: Evidence from U-Pb detrital zircon age distribution in “Timiskaming type” sedimentary rocks in the Island Lake greenstone belt, Superior Province, Canada

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Two distinct tectonic regimes have been proposed to have been operating in the Archean, vertical and horizontal (“modern style”) tectonics. Most authors see these as separate processes that would have operated exclusively from each other, although recent work has suggested that they could be contemporaneous and that the Neoarchean represents a transition from a time dominated by vertical tectonics to one dominated by horizontal tectonic processes (Lin, 2007, and references therein).

Studies on Archean greenstone belts can help to test these ideas, and this study investigates a clastic sedimentary package that is characteristic of Neoarchean greenstone belts, the “Timiskaming-Type” sediments. Traditionally these sequences are interpreted to have been deposited in strike-slip basins opened by horizontal tectonic processes. More recent studies have suggested that these sediments were deposited in inter-diapiric basins formed by vertical tectonic processes.

This study investigates the distribution of U-Pb detrital zircon ages within the Island Lake Group, a “Timiskaming type” sedimentary succession located in the Island Lake greenstone belt. The distribution of observed ages is distinct from unit to unit throughout the succession, and correspond to the ages of supracrustal and plutonic rocks in the belt. The data are consistent with a model that involves erosion down through a supracrustal pile in the early stage of basin formation and sedimentation followed by unroofing of plutons in the latter stages. The model presented here involves sagduction and diapirism processes that produce an inter-diapiric basin as a result of vertical tectonics.

Reference

A petrologic view of mantle geochemistry: Os and He evidence for ancient depleted mantle heterogeneities

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Osmium isotopes in MORB and OIB appear to give a very different picture of the chemical history of the mantle than traditional isotope systems such as Sr, Nd and Pb. In particular, Os isotopes suggest that depleted, harzburgitic heterogeneities persist in the both the OIB and MORB source for at least 2 Ga, much longer than generally suggested by Sr, Nd or Pb isotopes. Recent partitioning experiments imply that He isotopes also record ancient depleted heterogeneities in the mantle [1]. In this talk I will show that the He and Os records of mantle depletion agree very well, with both indicating large melting events at 1.2, 1.9 and 2.7 Ga, corresponding well with peaks in the age distribution of continental crust. The agreement of these two independent mantle isotopic systems with the crustal record of melting is strong evidence for large melting events in the Earth’s past.

Why don’t we see this history in Sr, Nd and Pb? One possible explanation is that the mantle is largely heterogeneous, consisting of 15-20% subducted basaltic crust (eclogite) set within a matrix of depleted olivine-orthopyroxene rich matrix (harzburgite). This is essentially the marble-cake model of Allegre and Turcotte [2], and is supported by seismic scattering results [3] showing about 17% of the mantle consists of 10 km sized heterogeneities (presumably the eclogitic components).

If so, the eclogitic components would contain nearly all of the Sr, Nd and Pb in the mantle, while the harzburgite matrix would contain most of the Os and He (and probably the other noble gases). The eclogitic components have low melting temperatures and would melt readily if brought into a mid-ocean ridge system. Those melts would form the oceanic crust, which would eventually be subducted, turn back into eclogitic heterogeneities, which would then melt in a ridge again... This is the cyclic, young history recorded by Sr-Nd-Pb, the history of enrichment. In contrast, the refractory harzburgite would not easily melt again, even if brought into a ridge system, and so should be quite persistent in the mantle. As these refractory heterogeneities are relatively inert, they should record the timing of ancient melting events more readily than isotopes in low melting temperature phases. Thus from a petrologic viewpoint, the difference in histories recorded by Sr-Nd-Pb versus Os-He may be a natural consequence of the different minerals in which they reside.

References
The hidden history of mantle depletion: Os isotopes reveal a link between mantle depletion and crustal growth

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Two recent studies [1, 2] have provided new arguments in favor of pulsed growth of the continental crust (CC), with the main growth periods at 1.2, 1.9, 2.7 and 3.3 Ga. These CC growth pulses should be recorded as melt-depletion events in the mantle, but are not seen in the isotopic systems most commonly used to study the mantle (Sr, Nd, Pb). It is likely that the depletion history of the mantle is ‘hidden’ from these systems due to the subduction of enriched oceanic crust. Osmium, on the other hand, is compatible during mantle melting, and is a robust recorder of the timing of mantle depletion [e.g. 3].

Here we present over 400 new Os isotopic analyses (by laser-ablation multi-collector inductively coupled mass spectrometry: LA-MC-ICPMS) of osmiridium grains from three locations (Urals, Tasmania and Tibet). The data show a recurring peak at a \(^{187}\text{Os} / ^{188}\text{Os}\) value of 0.12±0.01, corresponding to a mantle depletion age of 1.2±0.1 Ga, and matching the youngest of the proposed CC growth events. The 1.2 Ga peak is also present in published data on osmiridiums from Oregon, USA [4] and from whole rock analyses of abyssal peridotites. Mixing models confirm the position of the 1.2 Ga peak in all datasets, and Monte Carlo simulations indicate that the probability that this repetition is the result of random chance is less than 1 in 100,000.

The older events, at 1.9 and 2.7 Ga, also appear to be recorded in the Os data, though the number of data points is small. In sum, the Os isotopic composition of the mantle records global melting events that correspond to peaks in CC age distributions, confirming the episodic model of CC growth and planetary differentiation.

References

Irradiation of organic matter by uranium and thorium: From mineral deposits to extraterrestrial environments

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Many occurrences of solid organic matter in ore deposits are directly related to the distribution of uranium and thorium minerals. This relationship reflects a mutual precipitation: irradiation from the minerals causes polymerization and solidification of fluid hydrocarbons, and the organic matter can cause the concentration of uranium to the scale of an ore deposit. Irradiation progressively alters the organic matter, by dehydrogenation, oxidation, and increasing aromaticity, and also causes fractionation of carbon isotopes. Studies of this alteration in samples from mineral deposits are contributing to an understanding of how organic matter is processed by irradiation in a range of other environments, from hydrocarbon reservoirs to interstellar space.

Data from mineral deposits show two opposite trends of carbon isotope fractionation with irradiation. New experimental data explains this in terms of two distinct mechanisms: (1) a decrease in alkylation and increase in oxygenated compounds related to reactions of complex hydrocarbon mixtures with free radicals, and (2) increase in polynuclear aromatic hydrocarbon (PAH) size and alkylation due to polymerization from a methane-rich source. Both processes are expected to occur similarly in hydrocarbon reservoirs. The data also support a model for extraterrestrial PAH formation due to cosmic irradiation of simple hydrocarbons in interstellar ices, and more widely an improved understanding of the response of organic matter to irradiation will help interpret the organic compositions of carbonaceous meteorites, cometary ices, and icy moons such as Titan. As irradiation can result in increased molecular complexity and the precipitation of heavy compounds, it is possible that it played a role in the prebiotic chemistry essential as a prelude to the evolution of life.

On Mars, mineral radioactivity is relatively low but would still cause long-term damage to any microbial spores. Other forms of irradiation (solar, cosmic, UV) have a greater effect in the near-surface, and would severely alter or destroy any organic matter down to 3m depth.

References
Impact of earthworms on metal mobility and availability

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It has been suggested that earthworms may be of use in enhancing phytoremediation or alternatively that earthworms may enhance metal mobility at contaminated sites thereby increasing risk of exposure for receptors. In this study earthworms were cultivated for 28 days in two different metal contaminated soils at differing earthworm number to soil mass ratios. Swaledale soil contained 16 ppm Cd, 28 ppm Cu, 5164 ppm Pb, 3433 ppm Zn, 6 % organic matter, had a pH of 6 and a sandy texture. Wisley soil contained 5 ppm Cd, 110 ppm Cu, 910 ppm Pb, 260 ppm Zn, 10 % organic matter, had a pH of 5.4 and was a loamy sand. Earthworm number to soil mass ratios ranged from 1 :200 to 1 :5. After 28 days earthworms were depurated on filter paper and metal body burden was determined. Soil solution was extracted from soils using rhizon soil solution samplers and analysed for metals and dissolved organic carbon. Cold and hot water extractable carbon were measured on the soils. Soils were extracted with K2SO4 to estimate microbial numbers. The European 3-stage sequential extraction was applied to the soils.

Earthworm metal body burden and BCR Step 1 extractable metal decreased with increasing earthworm density. Metal and organic carbon soil solution concentrations and cold and hot water extractable soil C increased with increasing earthworm density. There were no significant changes in microbial activity with earthworm density.

The data are consistent with earthworm-derived organic compounds complexing metals and bringing them into solution off soil particle sorption sites. Thus metal concentration in soil solution and therefore metal mobility increases with earthworm density. However, the metals present as organo-metal complexes are not available for uptake by the earthworms so that metal body burden is unaffected or decreases, i.e. metal bioavailability decreases.

Corroded Magnox sludge and plutonium waste cementation

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Corroded Magnox sludge waste
Corrosion of spent Magnox fuel rods in water filled storage ponds has produced magnesium-rich sludges contaminated with fuel and fission products. We have experimentally investigated the composition and evolution of an inactive corroded Magnox sludge (CMS) simulant.

Our characterisation of the sludge using infrared spectroscopy, X-ray diffraction, and environmental scanning electron microscopy (ESEM) has determined that CMS is mainly composed of brucite, Mg(OH)2, and additionally artininite, Mg2CO3(OH)2.3H2O.

Plutonium association with CMS

It has been suggested that Pu adsorption onto CMS colloids may provide a mechanism to enhance Pu mobility. Therefore, we have determined the associative behaviour of plutonium in solution with CMS in a model storage pond/effluent treatment system. Using a full-factorial design, we have quantitatively determined the effects of CMS, and other components of the storage pond and effluent treatment system, on Pu solubility. This provides an important first approximation to true Pu solubility.

The addition of carbonate in solution had the largest influence over Pu solubility, allowing >90% of the Pu to pass through a filter membrane. The presence of CMS, and polyelectrolyte increased Pu filter hold-up. Silica at 1 ppm produced no observable effect. Solution pH was also found to have a significant influence over Pu filterability. Over the pH 7 to 11.5 range examined, more Pu was held up on the filter at higher pH.

Cementation of Pu contaminated CMS

For long-term storage it is intended that the CMS waste be immobilised in a cementitious wasteform. Our current research is intended to extend our understanding of the structure and behaviour of these cemented wasteforms. Our investigation of CMS evolution is continuing, and additionally we have begun to examine the microstructure of ordinary Portland cement (OPC) based samples. Our cement samples doped with CMS, Zr, U (and later Pu) have been analysed using SEM to establish the hydrated calcium silicate (CSH) phases present and with which phases the Zr and actinide elements associate. Further work will determine the evolution of these phases and co-ordination chemistry of the actinides. Eventually this data will be included with those from actinide leaching experiments to relate the cement microstructure with immobilisation performance.
Adsorption of heavy metal in contaminated surface water onto Limestone and Coconut Coir pith

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Geo-environmental studies were conducted in Katedan Industrial Development Area, Hyderabad, India, where the industrial effluents has contaminated the fresh water lakes.

To treat the effluent through a Permeable Reactive Barrier (PRB), the contaminated lake samples were collected to carry out the column tests in the laboratory to identify the appropriate reactive material to reduce the concentration of toxic/heavy metals like Lead, Zinc, Chromium, Arsenic, Copper etc. to an environmentally acceptable limit by their adsorption on to the reactive material.

The column experiment was conducted for one week to treat the contaminants in the surface water from Katedan Industrial Area using various reactive materials such as Zero Valant Iron, Coal, Limestone and other organic materials like Coconut coir pith, Hey, Cow dung cakes and plant materials like leaves, barks and stems etc.

The contaminated water was passed through the column made of Polyvinyl Chloride (PVC). The column is 50 cm long with diameter of 10cm. It was filled with 70% (14cm) height of 2-4 grain sized limestone and 30% (6 cm) of fibrous coconut coir pith.

The flow rate of 55 rpm was kept constant through out the column experiment. The effluents from the column were quantitatively analysed using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES).

The concentration of certain heavy metals at the effluent was reduced to the environmentally acceptable limits eg. (Cr 43.52 µg/kg to 21.49 µg/kg), (Cu 30.4 µg/kg to 4.62 µg/kg), (Ni 27.44 µg/kg to 12.54 µg/kg), (Pb 15.62 µg/kg to 9.92 µg/kg), (Zn 98.25 µg/kg to 0.80 µg/kg) by limestone and coconut coir pith. The limestone has helped in increasing the alkalinity of contaminated water passing through it up to pH – 9, the rise in alkalinity allowed the heavy metals to precipitate that in turn was adsorbed by the coir pith. The fibres containing lignin did remove the heavy metal ions showing that lignin does play a major role in metal ion sorption.

References

Electrical properties of geikielite at high pressures and temperatures

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Fe-Mg- titanates minerals (ilmenite, pseudobrookites, ulvospinel, geikielite, etc.) are common accessory minerals in terrestrial metamorphic and igneous rocks, and are especially abundant in the high-Ti environment of the lunar crust [1]. Study of high-pressure phase stability of Ti based minerals are considered to be most important in estimating, and extracting helium-3 from the moon’s regolith, because helium-3 gets trapped on the moon within Ti-rich glass particles, along with –geikielite-ilmenite crystal boundaries, and within moon dust [1]. Minerals with intermediate compositions of ilmenite–geikielite solid solution also known to occur as accessory mineral in kimberlites, with geikielite content ranging from 30 to 70 mol % [1,2]. Information on high-pressure phase stability of Ti –based oxides would provide a useful geobarometer for ilmenite-bearing rocks either shocked by a meteorite or exhumated from the Earth’s deep mantle. The electrical resistivity of nano-crystalline geikielite decreases from 2.246 X 10 ^8 Ω m at room pressure to 2.0 X10 ^6 Ω m at 7.8 G Pa, whereas the electrical resistivity of natural geikielite decreases from 1.098 X10 ^8 Ω m at room pressure to 1.74 X 10 ^5 Ω m 7.8 G Pa, indicating more compressibility of natural geikielite in the pressure range of investigations. The present shows that the geikielite does not undergo any pressure induced phase transition up to 7.8 G Pa, indicating its stability in the earth’s mantle pressure conditions [3,4].

References
Stalagmite records of tropical Pacific climate since the Last Glacial Maximum

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Long, high-resolution, well-dated paleoclimate records from the western tropical Pacific are scarce, obscuring the response of tropical Pacific climate to changes in global boundary conditions, abrupt climate changes, and external radiative forcing. Here we present three absolutely-dated stalagmite oxygen isotopic records from Northern Borneo that track fluctuations in Western Pacific Warm Pool hydrology over the last 27,000 years. Over 70 U-series dates and 11 isochrons provide excellent chronological control for the over 1200 stable isotope measurements. Our results suggest that rainfall in northern Borneo during the Last Glacial Maximum was similar to present. However, a pronounced maximum in stalagmite δ18O values occurs ~16.3 thousand years ago, consistent with dry conditions in the WPWP during the Heinrich 1 abrupt climate change event. The deglaciation is also marked by a 1000-yr-long oxygen isotope plateau centered at 13.2 thousand years ago that coincides with the Antarctic Cold Reversal, but there is no evidence for the Younger Dryas event observed in many other deglacial records. A broad minimum 5,000 years ago reflects the sensitivity of Warm Pool hydrology to spring/fall precessional insolation forcing. The new records demonstrate dynamic linkages between northern and southern high-latitude climate and tropical Pacific convection, and highlight the sensitivity of tropical Pacific convection to external radiative forcing.

Multiple redox states in the Archean-Proterozoic hydrosphere

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The late Archean deep water environments of Western Australia’s Hamersley Group Marra Mamba Iron Formation and Mount McRae Shale are characterised by extremely light organic carbon and relatively enriched, even positive, carbonate carbon δ13C values consistent with the presence of methanogens (Schidlowski, 2001). Positive mass independently fractionated (MIF) sulfur isotope values are found in fine-grained pyrite disseminated throughout these organic rich mudstones, while negative sulfur MIF is seen in rare pyrite nodules. This suggests that the fine-grained pyrite was formed abiotically, whilst the formation of the nodules was microbially mediated (Farquhar and Wing, 2003).

Multiple pyrite morphologies are not common in the Hamersley Group’s late Archean shallow water Wittenoom Formation; however, positive sulfur MIF in fine-grained pyrite in these dolostones suggests the absence of sulfate reducing microbes. The lack of very light organic carbon and positive carbonate carbon δ13C values implies that late Archean shallow water environments were too oxic to support anaerobic metabolisms, potentially in favour of more oxygen tolerant species.

Paleoproterozoic sulfur MIF in the Dales Gorge Member and Whaleback Shale of the Brockman Iron Formation Group shows good correlation between fine-grained and nodular pyrite in the same sample, both demonstrating either negative or zero MIF, regardless of depositional environment. Furthermore, organic and carbonate carbon δ13C trends toward more modern values. This suggests that after the Archean-Proterozoic boundary, both deep and shallow water environments were sufficiently oxic for sulfate reducing microbes and thus marks the transition to a more uniformly oxidised hydrosphere capable of supporting aerobic life.

References


Tailings oxidation and mineralogy of Haveri Au-Cu mine, SW Finland – Preliminary results

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The Haveri Au-Cu deposit, situated in SW Finland, comprises mainly of pyrrhotite, chalcopyrite and pyrite with accessory Fe-Co-Ni sulfoarsenides, sphalerite, molybdenite, iron oxides and native gold (Mäkelä, 1980). The tailings were piled during the active mining period from 1942 to 1961 covering ca. 18.5 ha and having an average depth of 7 meters.

In May 2006, a total of 40 profiles were drilled. Three profiles, and 17 tailings samples at intervals of one meter, were selected for mineralogical feasibility study. They were studied by optical reflected-light microscopy and by scanning electron microscope (SEM-EDS). Furthermore, the samples will be examined by X-ray diffraction (XRD), and geochemical analyses from selective leachates are planned.

The tailings are exposed to air, rainwater and meltwater which oxidize the primary sulfides remaining from the ore processing. Consequently, the tailings present zoning with oxidized vadose layer closest to the surface and unoxidized water-saturated layer below 3 to 4 meters. The uppermost vadose layer (from 0.9 to 2.0 m in thickness) contains primary iron oxides and scarce remnant sulfides, and abundant secondary Fe precipitates giving the characteristic ochreous color. Pyrrhotite and pyrite are the first sulfide minerals to oxidize and to dissolve. The geochemical processes within the surface layer of the impoundment produce acid mine drainage, in other words, acidic and heavy metal-rich waters. The secondary Fe precipitates (e.g. jarosite) form from the resulting solutions.

Deeper layers are under reducing and anoxic conditions presenting grayish black color. Here the major sulfides, pyrrhotite and pyrite, and minor chalcopyrite exhibit angular forms and no sign of alteration.

The oxidation process will continue for decades or even hundreds of years until reaching the groundwater surface.

The research is part of the EU LIFE Environment project “Risk Assessment and Risk Management procedure for Arsenic in the Tampere region” or RAMAS (www.gtk.fi/projects/ramas).

Reference

Chemical weathering of basaltic rocks in the tropical environment

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The chemical weathering of basaltic rocks under tropical conditions was marked with the generation of moderate to highly alkaline and reducing hot spring. Only a few similar occurrences has been reported in the Philippines where most of the hot springs are highly acidic and volcanic in nature. In Sira-an hot spring along the coast of Antique province, flammable gas (i.e. CH4(g)) accompanies the hot springs waters. Its pH, redox state, temperature, and dissolved constituents are considerably different from a nearby groundwater well and seawater such that it can be considered an anomaly. The mineral assemblage of the fracture fill materials comprises calcium-aluminum-silica-hydrate (CASH) phases, zeolites, and chlorite suggesting highly alkaline conditions.

The local hydrogeology of the area is responsible in the formation of the alkaline and reducing hot spring (Figure 1). Limestones at elevated areas dissolve to form dissolved calcium and carbonate enriched groundwater which percolates through the fractured basaltic rocks. Dissolution of minerals in the basaltic rock under anoxic conditions generates a highly reduced and alkaline aqueous conditions which converts the dissolved carbonate to methane. The dissolved components (i.e. Ca, Si, Fe, Al, Mg) in turn precipitates into CASH phases, zeolites and chlorite.

Figure 1. A schematic presentation of the alkaline and reducing Siraan hot springs, Antique, Philippines.
Arsenic and Mercury in brown and hard coals from deposits of Poland
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Problem of the environmental pollution by As and Hg emitted during coal combustion is important. The aim of the study was a determination of As and Hg concentrations in coals extracted in Poland and mostly burned there.

Material and methods
Concentration of arsenic and mercury have been determined in 250 samples of brown and hard coals from deposits of Poland. Hard coal samples were collected from Carboniferous Upper Silesian (USCB), Lower Silesian (LSCB) and Lublin Coal Basins (LCB) and brown coal samples were collected from mined deposits in Poland – Turów, Belchatów, Koźmin, Lubstów, Adamów and Kazimierz. Arsenic contents have been determined with the ICP-MS spectrometry and mercury contents by AAS method.

Results
The mean arsenic concentration in the hard coals is 16 mg/kg. Coals from LCB contain in average 47 mg/kg of arsenic, coals from LSCB – 61 mg/kg. In coals from USCB mean concentrations of As range from 2 mg/kg (NW part of the basin) to 20 mg/kg (SW part of the basin). The average As contents in brown coals is 9 mg/kg (Turów 29 mg/kg, Belchatów – 3 mg/kg, Konin-Adamów – 1 mg/kg). The average mercury content in the hard coal samples is 85 ppb. The mean Hg content in hard coal from the LSCB is 399 ppb, USCB 60 ppb and 105 ppb in coals from LCB deposit. Coals from the eastern part of USCB contain higher mercury concentration than coal from western part of basin. They might be caused by sulphide mineralization in Triassic dolomites overlying this part of USCB. The average Hg concentration in all tested brown coal samples is 322 ppb and it is four times higher than average Hg concentration in hard coals. The highest average Hg content in lignite is observed from Belchatów deposit - 416 ppb and the lowest - 199 ppb from Lubstów deposit. Coals from tectonic grabens are enriched in Hg in comparison with lenticular deposits which were not tectonically influenced.

Conclusion
Obtained results permit to estimate that about 28t/a of mercury and about 2000t/a of arsenic are excavated and emitted with hard and brown coals burned in Poland.

Melt mixing and crystallisation in the plumbing system of the 1783 Laki eruption
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The 1783 Laki fissure eruption of SE Iceland is the second largest basalt eruption in recorded history, extruding ~15km³ of lava and minor tephra over the course of 8 months and producing a notorious ‘dry haze’ of poisonous volcanic smog, leading to famine, disease and the death of 25% of Iceland’s population [1]. Large scale basalt eruptions are common in Iceland (e.g. Eldgjá, 934 AD and Thjorsa, ~8000 yBP; 19km³ and 21km³ respectively) and are fed by discrete batches of magma accumulating in large crustal reservoirs. The relationship between crystallisation and mixing in the storage reservoirs that give rise to such voluminous, long-lived eruptions has been the focus of recent SIMS analysis at the University of Edinburgh.

The concentrations of REEs and selected trace elements, including Zr, Y, Nb and Sr, were measured for 90 olivine-hosted melt inclusions from Laki using a Cameca 4f ion microprobe. The range of REE concentrations measured in the melt inclusions (representing discrete batches of parental melt) is not seen in whole rock compositions, implying that this variation is destroyed by mixing in the storage reservoir prior to eruption. Olivine compositions vary from Fo87 – Fo73, corresponding to a 50°C drop in crystallisation temperature. The standard deviation of La/Yb in melt inclusions hosted in olivine with Fo>85 mol% is 0.75 (n=40), but only 0.25 (n=16) in olivines with Fo<78 mol%, showing that cooling, and subsequent crystallisation of less forsteritic olivine, was therefore concurrent with mixing. The variation in La/Yb reflects variation in the composition of mantle melts being supplied to the crust under SE Iceland. A similar relationship between mixing and cooling has been found in a smaller, more primitive flow from northern Iceland [2], indicating that coupled mixing and crystallisation is common in the plumbing systems of Icelandic volcanoes.

References
Organometallic complexes from Ni-Mo-PGE black shales in South China – Combination of bioactivities, hydrothermal venting and phosphate deposition during global Cambrian biological explosion

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The study of organometallic complexes in ancient geological environments can explain mechanism of accumulation of metals and provide clues for the evolution of the earth life. For example, many synthesized complexes of aryl phosphines and aryl phosphites with platinum metals proved to have important mechanistic implications for homogeneous and heterogeneous catalysis.

Anomalous metal concentrations up to ore grade were reported from black shales that occur in different geological environments throughout the geological record. Besides major ore minerals and elevated metal concentrations in base metal sulfides, many authors suggested empirical relationship between various metals and organic matter.

Using HPCL-MS analysis, we found Co-, Cu-, Ni- and Pt-organometallic compounds in chloroform extract of organic matter from Ni-Mo polyelement sulfide ore bed hosted in lower Cambrian black shales whose organic matter was derived mainly from algae and cyanobacteria and whose formation coincided with the famous Cambrian biological explosion and world phosphate deposition. Beside organometallic compounds sulfur, polycyclic aromatic hydrocarbons and free-metal porphyrines were identified.

Our results demonstrate how biological activity was important for primary metal entrapment in hydrothermally enriched marine environment around medium temperature (< 300°C) hydrothermal vent in semi-restricted basin.

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Re-Os study of the Polish Kupferschiefer: Implications for source and timing of metal enrichment

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The age and genesis of world-class copper deposits of the Kupferschiefer-type have been a subject of much debate with proposed synsedimentary to postdepositional models. The 187Re-187Os isotope system has been successfully applied to generate whole rock isochrons in differently aged organic carbon-rich sediments.

Six samples of typically Cu-mineralized Upper Permian calcareous black shale and limestone of the Kupferschiefer type from the Lubin mining district (Poland) were studied for Re-Os isotopes, platinum group elements (PGE), and selected major and trace elements.

Mineralized black shales (Cuavg. = 4.9 wt.%, Agavg. = 242 ppm, Pbavg. = 138 ppm and Znavg. = 87 ppm) display low PGE values (Pt = <2 – 3.2 ppb, Pd = <2 – 2.8 ppb, Ru = <10 ppb, Rh = 0.4 – 5.2 ppb and Ir = <0.1 ppb) and c(Re) = 249.4 – 22174 ppb, c(Os) = 0.4831 – 1.0009 ppb and 187Os/188Os = 10.26 – 426.7. Lower base metal but comparable PGE, Re and Os values are typical for basal limestone. Calculated correlation coefficients indicate preferential Re affinity to Cu-sulfides and Os affinity to organic matter.

In a 187Os/188Os vs 187Re/188Os plot the entire data set defines an isochron corresponding to an age of 240 ± 3.8 Ma, which most likely reflect late diagenetic/epigenetic metal enrichment.

The initial 187Os/188Os ratio of 0.99 ± 0.22 is slightly less radiogenic but within the variation range of present-day seawater and excludes any significant contribution from hydrothermal/mantle or meteoritic PGE sources.

This work was financially supported by the EC in the frame of Bioshale European project (6th Framework program - NMP2-CT-2004-505710).
Three decades of Hf isotope research

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Following early experiments with the Lu-Hf system in the 1950’s to 1970’s, we established routine chemistry and TIMS measurement in 1980. TIMS Hf measurement is a “brute force” technique, involving use of a Re ionizing filament at the limit of its range. Practitioners can testify to the strain that high filament temperatures and high Re ion beams place on the ion source and collectors of the mass spectrometer. Nevertheless in this period many of the important areas of Lu-Hf isotopic studies were identified and developed. These included meteorites, crust-mantle differentiation, and the use of dated zircons to determine initial Hf isotopic signatures.

The advent of MC-ICPMS allowed analysis of up to 100 times less Hf, so that samples like chondrites and komatiites became truly accessible. High precision was obtained on small rare meteorites, and oceanic tholeiites could be analyzed in large numbers. ICP techniques also allowed a reduction of chemistry and much more rapid mass spectrometry. Somewhat intricate and/or empirical corrections needed to obtain accurate Lu and Hf data in ICP measurement are manageable. The large database now existing shows that Hf isotopic data do mirror patterns from Nd in many cases, but that Hf has considerable importance where behavior differs from Nd. Examples are oceanic sedimentation and mantle partitioning, particularly in higher-pressure mineral phases.

It seems inevitable that one of the main future applications of Hf will be in determination of initial $^{176}\text{Hf}/^{177}\text{Hf}$ in zircons U-Pb dated by laser MC-ICPMS. The initial Hf data are powerful in discriminating crustal sources, and the opportunity to acquire hundreds of Hf values is tempting. However, non-specialists often do not realize that 10 to 40% of the 176 mass signal has to be subtracted to remove Yb and Lu and arrive at the abundance of $^{176}\text{Hf}$. This is an enormous correction when epsilon-unit (i.e. 0.01%) variations of $^{176}\text{Hf}/^{177}\text{Hf}$ are the target. Intricate and empirical correction procedures are needed to account for differences in mass fractionation behavior of Yb, Lu and Hf, as well as the Er sometimes employed, and the accuracy of the 10-40% interference correction is critically dependent on these. Parallel analysis of zircon Hf by solution ICP has been employed in some critical studies, but this may not be practical for groups who measure large numbers of zircons, particularly detrital zircons. Probably, many who will measure and present laser Hf data for zircon will not be even partly specialized in isotope geochemistry. We must place a high priority on establishing robust, globally-agreed standards and procedures for laser Hf analysis of zircons.

Monitoring of atmospheric particulate matter around Raipur Central India

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The concentration, variations and sources of air borne carbonaceous particulate matters: volatile organic carbons (VOC$^{10}$, VOC$^{10-2.5}$ and VOC$^{2.5}$), nonvolatile organic carbns (OC$^{10}$, OC$^{10-2.5}$ and OC$^{2.5}$) and black carbons (BC$^{10}$, BC$^{10-2.5}$, and BC$^{2.5}$) in most polluted area of chhattisgarh Raipur have been studied for one year, June 2005-May 2006. The PM$_{2.5}$ and PM$_{10}$ samples were collected on pre-heated quartz fiber filters with the Partisol model 2300 Sequential Speciation Sampler (Rupprecht & Patashnick Co., Inc., USA) simultaneously. The combustion method equipped with the non-dispersive infrared detector (NDIR) is used for measurement of the volatile organic carbon (VOC), nonvolatile organic carbon (OC) and elemental carbon (EC) in the terms of CO$_2$. The annual mass concentration of PM$_{10}$, PM$_{10-2.5}$, and PM$_{2.5}$ was ranged from 62 – 975,17-602 and 20 – 373 $\mu$g m$^{-3}$ with arithmetic mean, median and STD values of 242, 139 and103; 222, 129 and 100; and ± 164.6,100.2 and 73.4 $\mu$g m$^{-3}$, respectively. The annual mass concentration of their carbons i.e. VOC$^{10}$, VOC$^{10-2.5}$, VOC$^{2.5}$, and OC$^{10}$, OC$^{10-2.5}$ and OC$^{2.5}$; and BC$^{10}$, BC$^{10-2.5}$ and BC$^{2.5}$ was ranged 2.1 – 47.9, 1.6 – 32.2, 4.1 – 80.2; 10.3-160 and 0.1 – 35.0, and1.6 – 23.1 and 2.6 – 65 and 4.6-123 $\mu$g m$^{-3}$ with arithmetic mean, median and STD values of 10.4, 12.3, 26.1, 48.8, 6.9, 7.9, 19.1, and 33.9, 6.7, 11.8, 25.6, 40.9, 5.0, 7.8, 17.2, and 30.7; and 9.8, 7.4, 16.5, 32.1, 7.4, 5.5, 14.0, and 25.6 respectively.

Keywords: particulate matters, carbonaceous particulate, Partisol model 2300 sequential speciation Sampler
Chemical and isotopic (C and S) composition of groundwaters from the Mt. Vulture volcanic system

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Mt. Vulture volcano is located in the most external part of the Apennine orogene (southern Italy), almost at the edge of the Apulian foreland. The volcanic activity occurred up to 130 Kys ago. The volcano is formed by a main feldspar-bearing series of pyroclastic rocks and subordinate lava flows, ranging in composition from basanite and foidite to phonolites (Schiattarella et al., 2005). Rare lava flows and dykes, with distinctly more silica-undersaturated composition melilitites, melilitte ankaratrites, and the ‘Melfi’ haiynophyre, were also emplaced. Carbonatite-melilitite magmas fed the final phase of volcanism producing maar-type craters. The large Na and S contents of the Vulture magmas (Marini et al., 1994) result in the widespread presence of sodalite-group phases among the feldespathoids (De Fino et al., 1982; Di Muro et al., 2004).

Most groundwaters are characterized by gas bubbling. In order to investigate the origin of solutes a total of 25 springs and wells were analyzed for the major and minor element contents, the isotopic composition of carbon in the total dissolved carbon (TDC) and sulfur in the aqueous sulfate. The chemical data suggest that the effects due to water-rock interaction are largely controlled by the input of CO₂ in the alteration processes. Kaolinite and smectite in different proportion have formed all along the east coast of India now preserved as discontinuous belt. Laterites could have formed all along the east coast adjoining Bay of Bengal. Lake sediments contain Be mostly from two sources; one deposited directly from atmosphere and adsorbed to the surface of the sediments and the other is in situ produced. The adsorbed Be have been used to estimate rate of sedimentation in the Kaluveli Lagoon. Most groundwaters are characterized by gas bubbling. In order to investigate the origin of solutes a total of 25 springs and wells were analyzed for the major and minor element contents, the isotopic composition of carbon in the total dissolved carbon (TDC) and sulfur in the aqueous sulfate. The chemical data suggest that the effects due to water-rock interaction are largely controlled by the input of CO₂ in the alteration processes. Kaolinite and smectite in different proportion have formed all along the east coast of India now preserved as discontinuous belt. Laterites could have formed all along the east coast adjoining Bay of Bengal. Lake sediments contain Be mostly from two sources; one deposited directly from atmosphere and adsorbed to the surface of the sediments and the other is in situ produced. The adsorbed Be have been used to estimate rate of sedimentation in the Kaluveli Lagoon. Most groundwaters are characterized by gas bubbling. In order to investigate the origin of solutes a total of 25 springs and wells were analyzed for the major and minor element contents, the isotopic composition of carbon in the total dissolved carbon (TDC) and sulfur in the aqueous sulfate. The chemical data suggest that the effects due to water-rock interaction are largely controlled by the input of CO₂ in the alteration processes. Kaolinite and smectite in different proportion have formed all along the east coast of India now preserved as discontinuous belt. Laterites could have formed all along the east coast adjoining Bay of Bengal. Lake sediments contain Be mostly from two sources; one deposited directly from atmosphere and adsorbed to the surface of the sediments and the other is in situ produced. The adsorbed Be have been used to estimate rate of sedimentation in the Kaluveli Lagoon. Most groundwaters are characterized by gas bubbling. In order to investigate the origin of solutes a total of 25 springs and wells were analyzed for the major and minor element contents, the isotopic composition of carbon in the total dissolved carbon (TDC) and sulfur in the aqueous sulfate. The chemical data suggest that the effects due to water-rock interaction are largely controlled by the input of CO₂ in the alteration processes. Kaolinite and smectite in different proportion have formed all along the east coast of India now preserved as discontinuous belt. Laterites could have formed all along the east coast adjoining Bay of Bengal. Lake sediments contain Be mostly from two sources; one deposited directly from atmosphere and adsorbed to the surface of the sediments and the other is in situ produced. The adsorbed Be have been used to estimate rate of sedimentation in the Kaluveli Lagoon.
Osmium groundwater flux from the Bengal basin: Implications for the osmium marine budget

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The Os residence time in the oceans is currently poorly constrained, in part because the sources of Os to ocean water have not yet all been explored. One such source, potentially important, may be groundwater flux. Basu et al. [1] suggested that Bengal Basin groundwater may provide a large flux of radiogenic Sr to the oceans. By analogy, and considering that the Ganges has the most radiogenic 187Os/188Os ratio yet measured in the world's rivers [2], groundwater of the Ganges alluvial plain may provide a significant flux of radiogenic Os to the oceans.

We present Os isotopic and concentration data for groundwaters collected along a traverse in the Bengal alluvial plain. As these waters are highly reducing, a specific method was developed (heating with CrVI in a high pressure asher, HPA-S at 250°C) to allow complete oxidation of all of the Os, and thus equilibration with the Os isotopic tracer. Oxidation at lower temperatures, in the HPA-S or in teflon vessels [3], led to underestimation of the Os concentration by as much as a factor of two.

Os concentrations are high (30-250 pg/l) and display 187Os/188Os ratios (2.2-2.6) in agreement with those of Ganges water and sediments. Os contents correlate strongly with those of Sr and several other elements, which allows us to roughly estimate the groundwater Os flux from the Bengal alluvial plain. Assuming conservative behaviour and both the mean Sr concentration and the groundwater flux of [1], we estimate an 188Os groundwater flux of ~ 9 M/yr. This estimate represents the MAR show that there are systematic changes in terms of εHf, εNd, and 87Sr/86Sr characteristics. In 176Hf/177Hf vs. Lu/Hf, 143Nd/144Nd vs. Sm/Nd, and 87Sr/86Sr vs. Rb/Sr spaces, the different segments define linear arrays. These arrays do not have any age significance but are mixing lines.

The central segment (A3) shows enriched mantle characteristics (εHf: -12.5; εNd: +7.5 to +8; 87Sr/86Sr: 0.70267 to 0.70277). Segment A2, located immediately to the north, has higher values in εNd (+10.2 to +11.7) and εHf (+13.2 to +14.5) but lower 87Sr/86Sr ratios (0.70244 to 0.70237). In contrast, the data from segments A1 and A4 define distinctive linear arrays. This involves a depleted end-member with εNd (up to +13), high εHf (up to +22), and low 87Sr/86Sr ratios (0.70244 to 0.70237) and an enriched end-member with low εNd and εHf and high 87Sr/86Sr ratios. Since there are no consistent trends with water depth or along axis position of the samples, sub-km scale mantle heterogeneities must be present beneath segments A1 and A4. The samples representing subaerial volcanism of Ascension Island mark the isotopically enriched extension of the linear array defined by MAR segments A1 and A4 (εNd: +6.8, εHf: +9.9; 87Sr/86Sr ratio: 0.70284). Samples from the submarine stage of Ascension Island are displaced towards higher εHf (+13.1 to +13.5), indicating that the volcanically dominated volcanic basement was fed from a distinctive, enriched mantle source. Hence, all of these observations imply that mantle material, representing the enriched end member component for segments A1 and A4, replaced the mantle domain responsible for submarine Ascension Island volcanism prior to the onset of subaerial volcanism (≤ 1 Ma). Altogether, these relationships argue against a mantle plume origin for Ascension Island.

Sub-segment scale mantle heterogeneity beneath the Mid-Atlantic Ridge near Ascension Island from combined Hf-Nd-Sr isotope evidence

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The Mid-Atlantic Ridge (MAR) between 7°30’S and 11°30’S shows prominent bathymetric along-axis variations with a shallow central part (segments A2 and A3) and deeply incised segments to the north and south (segments A1 and A4). These topographic variations are mirrored by a large compositional variations spanning the entire range of Atlantic MORB analyzed so far in εHf-Nd and εHf-87Sr/86Sr space. Ascension Island is located in the immediate vicinity (80 km west of the MAR), indicating voluminous off-axis partial melting in the mantle. We analysed near primitive samples (MgO> 5 wt%) for Hf-Sr-Nd isotope and trace element compositions and our data for the submarine and subaerial portions of Ascension Island and the different segments along the MAR show that there are systematic changes in terms of εHf, εNd, and 87Sr/86Sr characteristics.

References

Thallium in brown and hard coals of Poland

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Introduction

Main anthropogenic source of thallium in the environment is high-temperature processing of raw materials, in which it occurs at small concentrations.

Material and methods

Concentration of thallium and Ag, Cu, Pb, Rb and Zn contents have been determined in 214 samples of brown and hard coals with the ICP-MS spectrometry. Hard coal samples were collected from Carboniferous in Upper Silesia (USCB), Lower Silesia (LSCB) and Lublin Coal Basins (LCB) areas, and brown coal samples were collected from mined deposits in Poland – Turów, Biełchatów, Koźmin, Lubstów, Adamów and Kazimierz.

Results

Contents of thallium in brown coals ranges from 0.2 mg/kg (detection limit) to 2.4 mg/kg. It was noticed that coals from Biełchatów and small town Adamów-Konin region deposits - Koźmin, Lubstów, Adamów, and Kazimierz characterize very low concentration of thallium. In these coals Tl contents not exceed 0.4 mg/kg and average contents is <0.2 mg/kg. Turów deposit coals distinguish by increased Tl contents. Thallium concentrations in brown coals from theses deposits average 0.7 mg/kg. Distinctly higher Tl contents in Turów deposit coals are caused by overall lithology of the sedimentation basin and its alimentation area and may be connected with cropping up granites and granitoids of crystalline basement and Tertiary alkali basalts. High correlation between Tl and Rb concentrations in brown coals was observed.

Contents of thallium in hard coals ranges from 0.2 mg/kg to 5.3 mg/kg. Samples of hard coals from USCB characterize higher thallium concentration in comparison to two others coal basins. Average concentrations of that element in USCB coals is 0.5 mg/kg, whereas in samples from LCB is 0.4 mg/kg and in samples from LCB is 0.3 mg/kg. Our results shows diversification of thallium contents in coals from USCB. The highest concentrations were observed in coal from upper seams of SE part of the deposit. They might be connected with Zn-Pb (and Fe sulphide) mineralization in Triassic dolomites overlying this part of USCB. In these coals the high correlation between Tl and Pb contents was observed, and somewhat smaller correlations were noticed with Ag, Cu and Rb.

Conclusion

Obtained results permit to estimate that about 60t/a of thallium are excavated with hard and brown coals in Poland.

Hydrogen abundance in the prebiotic atmosphere. Reducing or weakly reducing?

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The atmospheric hydrogen abundance was crucial for the organic synthesis on the prebiotic Earth. For decades a common assumption of the fast (diffusion-limited) hydrogen escape lead to a belief that the prebiotic atmosphere had to be weakly reducing and therefore organic synthesis should have occurred only in the special locations such as hydrothermal vents.

However, the recent study of the hydrodynamic hydrogen escape from the anoxic hydrogen-rich planetary atmospheres suggested that hydrogen could have been lost at a very slow rate and a hydrogen-rich (reducing) prebiotic atmosphere could have been maintained by a reasonable volcanic hydrogen source. This calculation was incomplete though because we did not show how the atmosphere could get to the hydrogen-rich state in the first place.

Here we will report on the atmospheric conditions under which the hydrodynamic escape had to occur. We found that the switch between the reducing and weakly reducing atmosphere was a strong non-linear function of the ancient solar ultraviolet (UV) flux.

UV fluxes > 5 times the present UV flux favor the fast diffusion-limited escape and cause the atmosphere to be weakly reducing. UV fluxes < 3 times the present UV flux always result in a slow hydrodynamic escape and the hydrogen-rich atmosphere should be expected. We conclude that the rate of the organic production on the prebiotic Earth could have been directly dependent on the evolution of the UV flux of the ancient Sun.

We will also report on how the rate of the hydrogen escape would have changed when the first biosphere would provide a significant methane source in the Archean atmosphere.
Investigating the biogenic synthesis of chalcogenide-based nanomaterials

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The future of materials science is closely linked to nanotechnology and, as such, there is a need to improve the manufacture of nanomaterials in terms of environmental and economic impact. Using the capability of microbes to manufacture potentially useful bioanominalmers offers new methods of material synthesis that eliminate toxic organic solvents, minimize expensive high-temperature processing and can involve the use of industrial waste as the starting material, thereby incorporating a remediation step.

This research involves (i) identification of biomolecules associated with different bacterial strains that act as templates to direct bioanominalmer nucleation and growth; (ii) investigation of enzyme-mediated electron transfer reactions resulting in precipitation of nanoparticles; (iii) harnessing and scaling up these processes for biomimetic materials synthesis.

The biotransformation of selenium and tellurium oxyanions by four diverse organisms (Veillonella atypica, Bacillus selenitireducens, Geobacter sulfurreducens and Geobacillus stearothermophilus) has been selected as a model system to study bioanominalmer formation by a range of reduction processes. These organisms produce size- and shape-constrained Se/Te nanoparticles with different structural and spectral characteristics to their chemically formed counterparts (Fig. 1)(1).

Figure 1: Biogenic Se and Te nanoparticles

The elemental Se/Te is then further reduced to form reactive selenide/telluride, which is precipitated to produce chalcogenide-based fluorescent nanoparticles, such as CdSe.

Reference

Factors controlling 14C contents of organic compounds in oceans and sediments

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Fourteen years ago, Hayes published a review entitled “Factors controlling 13C contents of sedimentary organic compounds: Principles and evidence” (Hayes, 1993). It described four processes governing the distribution of the stable isotopes of carbon in individual molecules: “(1) the carbon source utilized, (2) isotope effects associated with assimilation of carbon…, (3)…effects associated with metabolism and biosynthesis, and (4) cellular carbon budgets”. To a first-order approximation, only the first of these would apply in an analogous discussion of “factors controlling 14C”. The 14C content of organic samples is reported in terms of fractionation-normalized values of Δ14C or fm (fraction modern). This practice erases all of the biosynthetic fractionations discussed above. Compound-specific 14C (CSRA) approaches were developed in part because of this apparent simplicity: values of Δ14C for individual compounds should depend only on the 14C content at t = 0 and radioactive decay since then. Calibration records determine 14C/12C ratios at t = 0, in principle allowing calculation of absolute chronologies. However, this applies only to organic matter produced directly from fixation of atmospheric CO2; biosynthetic reactions that draw upon other pools of the carbon cycle automatically begin with the imprint of a “reservoir correction”. In practice, this means that the value of Δ14C rarely = 0 at t = 0. Now, after more than ten years of CSRA, it is becoming apparent that reservoir correction is just one of several challenges facing the application of individual-compound measurements. These challenges can be classified broadly as analytical or interpretational. Problems of analysis include: (1) difficulty obtaining adequate quantities of sample, (2) tedious laboratory separations, (3) in the case of prokaryotic metabolism, uncertain contributions of presumed planktonic molecules by deep-pelagic or benthic populations. Despite the challenges, there have been numerous, successful applications of CSRA. Here I will show several recent examples from the literature and discuss how further work promises to illuminate new information about fluxes and residence times throughout the global carbon cycle.

Reference
Sr isotopic compositions of ultra-deep inclusions in diamonds: Implications for mantle chemical structure and evolution

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Recent models of mantle convection combined with seismology have caused a paradigm shift in Earth Sciences away from two-layered convection of the mantle, towards models that involve convective stirring throughout most of the mantle depth. Such models are now being supported by a variety of new geochemical data. This makes the study of our only samples of the lower mantle, ultra-high pressure inclusions in diamonds, imperative as one of the few ways of directly testing predictable outcomes of these models.

To do this we have applied ultra-low blank Sr isotope chemical techniques along with carbon isotope analyses to a suite of diamonds from the Rio Soriso, Mato Grosso, Brazil to investigate the isotopic characteristics of the lower mantle. The suite of diamonds were kindly supplied by Dr F. Kaminsky and contain inclusions of Mg-silicate perovskite (MgSiO₃), Ca-silicate perovskite (Ca-Pv; CaSiO₃) and ferropericlase, among other minerals. Ca-Pv inclusions contain several hundred to >1000 ppm Sr making it possible to analyse small inclusions of this mineral for their Sr isotopic composition, hence providing the first reliable Sr isotope determinations for the lower mantle environment. Our technique also allows determination of trace element compositions, including rare earth elements.

Two Ca-Pv inclusions have Sr isotopic compositions significantly less than the model “Primitive Mantle” ⁸⁷Sr/⁸⁶Sr composition (~ 0.7045) suggested for the lower mantle in two-layer convection models. The values obtained overlap with the MORB compositional spectrum which is taken as reflecting the long-term depletion history of the upper mantle. We interpret the Sr isotope results to indicate that the lower mantle, at the depths sampled by inclusions within diamonds, is not distinct from the upper mantle in terms of its Sr isotope composition. Carbon isotope data for these ultra-deep diamonds will also be presented to examine differences between “shallow” mantle carbon and ultra-deep carbon.

Mass bias: A comparison of solution and laser ablation MC-ICPMS

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The development of in-situ isotope ratio measurements using LAM-MC-ICPMS has proceeded steadily over recent years. To date the most widely used technique is the analysis of Hf isotopes in zircon and this application is now undertaken in many laboratories around the world. Other radiogenic isotope systems (e.g. Sr, Nd, Os, Pb) have been successfully measured in a variety of minerals but despite the demonstrated significance of spatially resolved measurements, these in-situ methods remain relatively restricted in their application. The main limitations (in accuracy and precision) are the trace-level abundance of the elements of interest and the magnitude of isobaric overlap corrections related to parent/daughter ratios. In-situ analysis of ‘non-traditional’ stable isotopes has not progressed as far as the radiogenic systems and this is mainly due to a lack of understanding of the processes that contribute to isotopic fractionation during ablation and in the plasma.

Recent studies have demonstrated that the origin of isotopic fractionation in LAM-MC-ICPMS is the result of a combination of laser- and ICP-induced fractionation. Whereas internal normalization using stable isotope pairs is able to account for the effects of these processes for radiogenic systems, the in-situ analysis of mass dependent stable isotopes requires careful standard-sample bracketing techniques using matrix-matched materials. The isotopic compositions of different aerosol particle size fractions of Cu metal show an enrichment of up to 0.5 per mil of the lighter ⁶⁵Cu isotope in the sub-250 nm particles. Isotopic fractionation is further enhanced by preferential ionization of the lighter isotopes from incompletely vaporised particles in the ICP. Analysis of Mg isotopes in olivine (Fo 92) indicates that there is no change in particle size distribution with ablation time and points to the influence of the ICP on isotopic fractionation.

The aims of this study are to provide a framework to understand the parameters and processes that control mass bias in the ICP, especially the differences between solution (wet) and laser (dry) plasma. A series of experiments has been carried out to investigate the contribution of plasma power, extraction voltage, gas flow, torch position, gas composition (Ar±He), sample matrix, and plasma loading on mass bias. Results will be presented for light, middle and heavy mass isotopic systems (e.g. Mg, Cu, Sr, Hf).
Ni signatures from the Dales Gorge Member of the Hamersley Group, Australia: Constraints on the origin of Banded Iron Formations

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The deposition of Precambrian banded iron-formations (BIFs) has been linked to significant compositional changes in the Earth’s atmosphere hydrosphere, and biosphere. Previous geochemical studies have measured the isotopic composition and the concentration of major, trace and rare earth elements in BIFs. Those studies have focused on the source of the metals (Fe, Mn, and Si) but others also have considered the role of the microbial activity and the nature of the primary precipitates. In this study we present the results of microscale geochemical analyses, coupled with high-resolution petrography, with the aim of establishing the controlling factors in the source and distribution of trace elements in BIFs.

As primary precipitates, hydrous amorphous silica would have crystallized as pure chert and cationic silica gels as siderite and greenalite, the latter entirely transformed into ferroan-talc. In addition, ferroan-talc is arguably a reaction product of siderite and chert. The presence of platy hematite is accompanied by an increase of ferroan-talc and a diminished siderite content. There is no evidence of magnetite as a primary precipitate, rather, it tends to occur as overgrowths on platy hematite. Early diagenetic apatite and late diagenetic ankerite-ferroan dolomite crystals constitute the remaining mineral phases.

We conclude that the distribution and concentration of trace elements in different mineral phases were influenced by hydrothermal activity. Considering the high concentration and strong correlation with Fe, it is suggested that Ni represents a reliable indicator of element contribution from hydrothermal vent systems, which is consistent with previous models based on REE and Nd isotopic signatures. Furthermore, by comparing the Ni:Fe ratios of the Dales Gorge Member with other major BIF types (Algoma-, Superior-, and Rapitan-type), it appears that hydrothermal input was a major source of some trace metals to the BIF depositional setting, particularly Ni.
Mineral chemistry of pyrochlore in residually inherited Fe-P-Nb-laterite ore bodies at Sokli carbonatite complex

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The Sokli carbonatite complex in Northern Finland has undergone extensive laterization and a vertical profile through the sequence varies from 0 to 70 metres. It contains a partially weathered saprock, saprolite, laterite covered by glacial deposits. The laterite is strongly enriched in phosphate, niobium and tantalum.

Locally the weathering profile is covered by a black Fe-P-Nb-REE enriched bed, 5 – 30 mm thick, which is situated directly beneath the glacial deposits and is interpreted to be residually inherited.

The residual bed contains pyrochlore which deviates texturally and chemically from the pyrochlores in main laterite and in fresh rock by being smaller (20µm) in diameter and by their euhedral crystal habit. These grains typically contain high density of fluid inclusions. SEM-EDS and microprobe study indicate that A-site occupancy is dominated Ca and Na of the pyrochlore structure while, along with the weathering, those two ions are detected to become partially replaced by K, Sr, Ba in laterite profile. Contradictory to the pyrochlores in fresh carbonatite-phoscorite and in laterite profile, the pyrochlore in residual bed lack uranium and has extremely low contents of thorium.

The role of Iron redox cycling for the natural acidification of ground water

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In wide areas of Western Australia (WA) springs are occurring that release acidic ground water (pH<3) into gypsum-rich playas. The origin of the acidity is related to the oxidation of Fe(II) and the subsequent precipitation of ferric (hydr)oxides (McArthur et al, 1991). The similarity of these systems to acidic mining lakes (AML) is striking. AML are forming upon oxidation of Fe(II) and sulfate-rich ground water, the pH typically ranges between 2.7 and 3.3 and is buffered by the solubility of schwertmannite (Regenspurg et al., 2004). Acidic conditions in AML are stabilized by an acidity-driven iron cycle at the sediment-water interface, where oxidation and reduction of Fe balance each other with respect to the alkalinity budget (Peine et al, 2000).

We therefore determined Fe(III) reduction rates, Fe(III) mineralogy and the Fe(III) reducing microbial community at three sites from iron-oxide rich (up to 7 % dithionite extractable Fe) soil material fully saturated with acidic ground water. The maximum Fe(III) reduction rate was 4.8 nmol g⁻¹ h⁻¹, a value similar to AML. Jarosite was the only Fe(III) XRD detectable mineral, schwertmannite appeared to be missing. The occurrence of Acidiphilium cryptum, an acidophilic Fe(III)-reducing bacteria could be proved. These observations suggest that also in the acidic ground waters an acidity driven iron cycle exists. They further imply the question how such a low pH can develop in a system that, contrary to AML, is not affected by pyrite oxidation.

Significant acidification from Fe(II) oxidation occurs only, if the corresponding anion originates from a strong acid, such as sulfate. Fe(II) in the ground waters from WA are regarded to be generated during weathering of Fe(II) bearing minerals and/or reductive dissolution of Fe(III) minerals. Both processes, however, generate HCO₃⁻ as the corresponding anion. We therefore postulate that HCO₃⁻ has been replaced by sulfate through the dissolution of gypsum and deposition of CaCO₃ as so-called calcrites:

\[ \text{Fe(HCO}_3\text{)}_2 + \text{CaSO}_4 \rightarrow \text{CaCO}_3 + \text{FeSO}_4 + 2 \text{H}^+ \]

References
**Microbial mobilization / volatilization of selenium sorbed on soil minerals**

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Selenium has major nutritional and biological function but the range between essential and toxic concentration is very small. The more toxic Se(IV) and Se(VI) are water soluble and hence bioavailable. The iron oxide and clay content of soils can affect the bioavailability through adsorption reactions, whereby Se(IV) is stronger adsorbed than Se(VI) [1]. The most reliable natural attenuation process of enriched Se in the environment is microbial methylation [2].

In order to investigate the alkylation / methylation process, *Alternaria alternata*, known as a Se resistant and active methyllating saprophytic fungus [3], was used for incubation studies. First we observed the alkylation of dissolved inorganic selenium (SeO\(_3^{2-}\), SeO\(_4^{2-}\)) and found different alkylated species over a wide pH range. Then, different selenium enriched minerals, e.g. goethite enriched by SeO\(_3\) alkylated species over a wide pH range. Then, different

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**Speciation of Cd, Cu and Pb by DPASV in unpolluted soil solutions**

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The mobility and the bioavailability of trace elements in soils are largely dependent upon their interactions with various organic and mineral ligands. These interactions control trace metal concentration and speciation in complex geochemical systems. The aim of this work is to determine the chemical speciation of cadmium, copper and lead in subsurface waters circulating in an unpolluted soil (Planosol). The study area is located on the Aigurande plateau in the northern part of the Massif Central (France). The substratum is composed of Paleozoic gneiss and intrusive granitic rocks. Soil solutions were collected in a gravelly and concretion-rich horizon (Fe- and Mn- oxyhydroxides) from 2004 to 2006 during the soil saturation period.

Chemical speciation of Cd, Cu and Pb was obtained by titrating the filtered water samples using differential pulse anodic stripping voltammetry. Cd, Cu and Pb have been chosen principally because of their various behaviours in the soil solutions. The aim of these experiments is to determine the apparent stability constant K and the corresponding ligand concentration (i.e. complexation capacity CC) using graphic method and the linear transformation method described by Ruzic (1982). A 1:1 complexing model was applied for result interpretation. Polarographic curves of Cd and Cu show significant peaks which may be associated with metal complexes. However, the copper titration curves underline different processes (complexation, adsorption and both processes) and provide evidence for “slow” kinetic reactions (in the experimental conditions). The cadmium titration curves show complexation processes and fast kinetic reactions. Results for measurement of complexation parameters are differently discussed for both metals. To evaluate the copper potential binding in all cases, potential distribution coefficients (Kd) are calculated based on (1) the estimation of K (complexation processes) and (2) the estimation of the number of sites available for metal association using potentiometry (adsorption processes). Potential Kd indicate that copper has a stronger affinity for complexation processes on organic compounds than adsorption processes. No significant seasonal variation pattern in the potential Kd parameter is observed. For cadmium, CC and K results show seasonal evolutions which can be linked to soil solution modifications and/or presence of various ligands. Pb experiments are actually in progress.

As a conclusion, voltammetry data give evidence about relationships between trace metals, organic matter and soil compounds.
Rates of weathering rind formation from $^{238}\text{U}-^{234}\text{U}-^{230}\text{Th}$ chronometry: Application to basalt weathering

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Weathering rinds developed on fresh rocks provide an opportunity to constrain the processes and rates of weathering as a function of parameters such as lithology and climate [1]. Such information requires first to develop reliable dating methods for such materials, which have been rarely studied, up to now, by radiochronometric techniques. In this study we propose to evaluate the potential of $^{238}\text{U}-^{234}\text{U}-^{230}\text{Th}$ chronometry to constrain the age and the formation rate of weathering rinds. We worked on a rind developed on a basaltic clast from a Costa Rican alluvial terrace, which has been extensively studied for mineralogy, geochemistry and petrology [1]. Nine subsamples of this clast were collected along a 2 cm transect, from the center of the fresh basalt core to the outer rind boundary, by drilling samples (2.5mm in diameter and 5mm depth) on one section of the split clast. Major and trace element concentrations, as well as Sr isotope ratios and $^{238}\text{U}-^{234}\text{U}-^{230}\text{Th}$ disequilibria have been analysed in each subsample. The data are consistent with immobility of Th and removal of mobile elements such as Ca, Mg, and Sr during weathering. Additionally, the increase of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios, ($^{238}\text{U}/^{235}\text{U}$) activity ratio and U/Th ratios from the fresh core to the outer rind boundary implies an input of U, with ($^{238}\text{U}/^{235}\text{U}$)$>$1, and an input of radiogenic Sr into the rind. These U and Sr inputs could both be ascribed to an external flux of dissolved U and Sr transported by the upper soil waters and adsorbed on or incorporated into Fe-Al oxy-hydroxides. Modelling $^{238}\text{U}-^{234}\text{U}-^{230}\text{Th}$ disequilibria in the rind by using an U gain-and-loss model classically applied for the interpretation of U-Th data in weathering profiles [2] give an advance rate of 4mm/10ka for this 1.5cm-thick rind. This age is in close agreement with other independant methods [1]. This study highlights the potential of the U-series dating method to constrain the timescale of weathering rind formation and therefore to provide new information about the rate of bedrock conversion to saprolite.

References

Tracking mobile niobium in the boreal environment with a “multi-survey” approach

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Niobium is mainly found in weathering-resistant minerals and generally considered as an immobile element and a recent soil (Echevarria et al 2005) and hydrochemical (Lutfi et al 2007) study has not changed this view. Still very little is known about the behaviour of Nb in various soils or in continental surface- and ground water environments. Nb has one stable ($^{94}\text{Nb}$) and several unstable isotopes found in radioactive wastes, e.g. $^{95}\text{Nb}$ and $^{98}\text{Nb}$ ($t_{1/2}$=354 and 2400a).

We examined dissolved and acid-available particulate fractions of Nb in boreal stream and ground waters and “non-detrital” Nb in sediments. The data consists of both speciation experiments and time–series of a small stream, large scale regional geochemical data sets and brackish/lacustrine environment sediments. In streams spatial patterns, temporal trends and speciation experiments all point to dissolved humic substances and colloidal Fe as the main carriers and controls of Nb. Clay-silt and ore deposits may be responsible for producing local stream-water Nb anomalies. In groundwater in glacial till overlying Proterozoic granitoids, dissolved (0.45 µm) Nb concentrations were about an order of magnitude higher than in stream water and strongly correlated with dissolved Fe. In the brackish-water sediments, the Nb concentrations (1.3-4.2 ppm) were clearly higher than in the lacustrine ones (0.25-0.53 ppm). To explain this, we assessed the potential role of organic material, biological processes, mineralogy and input factors. However, no satisfactory explanation for the change was found.

The use of multiple surveys was a successful approach for studying the behaviour of Nb. Although this metal is relatively immobile our results show that certain conditions favour Nb enrichment in the aquatic environment which also has implications for the behaviour of radioniobium.

References
Influence of transition metal cations on the formation and reactivity of biogenic Mn oxides

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Microbial manganese oxidation is the dominant pathway for Mn oxide precipitation in many environments. Several strains of \textit{Pseudomonas putida}, a common soil and freshwater bacterium, oxidize soluble Mn(II) via a multicopper oxidase enzyme, producing a poorly-crystalline layer-type Mn(IV) oxide, which is deposited in matrix of extracellular polysaccharides. These reactive nanoparticles have a remarkably high sorption capacity for metals due to their large surface areas (100 - 220 m\textsuperscript{2} g\textsuperscript{-1}), permanent structural charge (~16% Mn(IV) vacancies), and redox activity.

Our research is directed towards understanding the formation of biogenic Mn oxide minerals in metal-contaminated environments and their capacity to immobilize metals during active microbial precipitation. We have determined the effects of varying concentrations of cobalt, nickel, copper, and zinc on rates of bacterial growth and kinetics of enzymatic Mn(II) oxidation by \textit{P. putida} GB-1. In addition, we have applied X-ray absorption spectroscopy and X-ray diffraction to probe the mechanism of metal sorption to the biooxide-biofilm assemblages. The results from these experiments are interpreted in light of sorption experiments performed with freshly precipitated biogenic Mn oxides.

This work elucidates the dynamic and complex interactions between aqueous species, oxide minerals, and microorganisms encountered in natural systems. The results from this research have important implications for determining the role of biogenic manganese oxides in regulating the concentrations and distribution of trace and contaminant metals in aquatic and soil systems.

Petrology and \textit{P-T} path of the Guyang mafic granulites: Implications for tectonic evolution of the Western Block of the North China Craton

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In the last few years, two Paleoproterozoic continent-continent collisional belts, named the Trans-North China Orogen and Khondalite Belt have been recognized in the North Chia Craton. The Khondalite Belt formed by the collision between the Yinshan Block and the Ordos Block to form the Western Block at ~1.92 Ga, which then collided with the Eastern Block to form the North China Craton along the Trans-North China Orogen at ~1.85 Ga. In the last few years extensive investigations have been carried on the granulite-facies rocks in the Eastern Block, Trans-North China Orogen and Khondalite Belt, but few studies have been done on the late Archean granulites in the Yinshan Block. In this study, we present detailed textural and compositional data for various symplectites or coronas observed in the mafic granulites from the Guyang Complex in the Yinshan Block.

Petrological evidence from the Guyang mafic granulites indicates four stages of metamorphic evolution (M1 to M4). The M1 assemblage is preserved as mineral inclusions within minerals of the peak assemblages, represented by hornblende + plagioclase + quartz ± biotite in the mafic granulites, with \textit{P-T} conditions of ~0.6 GPa and ~750 ºC. The M2 assemblage is represented by orthopyroxene + clinopyroxene + garnet + plagioclase + quartz at 8.0-10.0 kbar and 800-900 ºC. The M3 assemblage is characterized by garnet+quartz or garnet+clinopyroxene symplectic coronas surrounding orthopyroxene, clinopyroxene and plagioclase grains, with \textit{P-T} of 9.0-10.0 kbar and 700-750ºC. The M4 assemblage consists of cummingtonite + plagioclase replacing clinopyroxene and orthopyroxene. These assemblages and the estimated \textit{P-T} conditions indicate that the Guyang mafic granulites underwent medium-pressure granulite-facies metamorphism with an anticlockwise \textit{P-T} path involving near isobaric cooling following peak metamorphism, which reflects a metamorphic event related to the intrusion and underplating of large amounts of mantle-derived magmas rather than a continent-continent collisional environment.

Acknowledgments

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Climate fluctuations during the last 3000 years in Guizhou, China: Evidence from the TIMS-U series ages and oxygen isotope composition of stalagmite

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The TIMS-U series ages and the δ^18O values of stalagmites from the Qixing Cave, Guizhou (26°4′30″N, 107°16′E) have been determined using the MAT-262-RPQ and Delta-S mass spectrometers. The results indicate that the stalagmite was deposited during the period of 3145-200 a B.P. and experienced four stages of the climate-environmental change.

(1) The first stage is in the range of 3145-2927 a B.P., which has δ^18O values from −5.61 to −5.16‰. This stage corresponds to the late Megathermal Period (7-3 ka B.P.);

(2) The second stage is in the range of 2927-1196 a B.P., which has δ^18O values from −5.51 to −4.59‰. Those values are higher than that in the first stage, indicating that the climate has become colder and dryer;

(3) The third stage is in the range of 1196-545 a B.P., which has the δ^18O values from −5.98 to −3.92 ‰. This stage corresponds to the Medieval Warm Period (MWP);

(4) The fourth stage is in the range of 545-200 a B.P., which has the δ^18O values from −5.39 to −3.51‰. It had the coldest and driest climate during the period of last 3000 years. This stage corresponds to the Little Ice Age from 1555 A.D. to 1800 A.D.

A regressive equation δ^18O (‰) = −2.20x10^-4 year (a B.P.) - 4.54 by fitting the two data sets of the δ^18O values and the age (years). It indicates that the δ^18O values become higher from 3145 a B.P. to 200 a B.P. which corresponds to lower precipitation. The warm and wet climate in the late Megathermal Period changed to the cold dry climate in the Little Ice Age. It is interesting to note that on the basis of the climate records during 1951-2000 A.D. measured at the Guiyang Meteorological Observatory (26°35′E, 106°43′N), two regressive equations of the temperature values and the age (years), the precipitation values and the age (years) have the negative slopes, implying that the temperature gradually decreases with an amplitude of −0.2°C and the precipitation gradually decreases with the amplitude of −7 cm during the last 50 years. Thus, the modern climate pattern in Guizhou Province, China, may be continuing from the last 3000 years.

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Mass-independent sulfur isotopes trace magma-wall rock interactions in the Bushveld Complex

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Abundant metasedimentary xenoliths in the Platreef, the ore horizon of the northern limb of the Bushveld Complex, South Africa, suggest significant interaction between the Bushveld magma and the surrounding country rock during emplacement. Fluid-mediated concentration of Platinum Group Metals and sulfur into the Platreef ore zone likely occurred as a result of this interaction. We use measurements of 33S/32S and 34S/32S to test hypotheses of material transfer between the Platreef and the surrounding country rock.

Solid-earth fractionation processes of 34S/32S and 33S/32S are mass-dependent, characterized by: δ33S = 0.515 x δ34S. Deviation from mass-dependent isotopic fractionation is quantified as ∆33S (= δ33S–1000*(1+ δ34S/32S))‰). Proxies for ‘primary’ igneous sulfur (meteorites, peridotite xenoliths) possess ∆33S values near 0 ‰. Similarly, relatively pristine Bushveld igneous rocks have ∆33S values ≤ 0.2 ‰. On the other hand, sedimentary country rocks surrounding the Platreef exhibit substantial non-zero ∆33S values. As ∆33S is a chemically-conservative tracer, non-zero ∆33S values in Platreef sulfide ore minerals are an indication of material transfer from the surrounding country rock.

We have performed a S isotope study along two profiles through the Platreef into underlying metapelitic and metacarbonate country rocks. In both profiles, far-field igneous rocks have have ∆33S values ≤ 0.2 ‰, while far-field metasedimentary rocks have significantly mass-independent S isotope compositions (∆33S ranging up to ~0.9 per mil in the pelitic rocks and up to ~5.0 per mil in the carbonate rocks).

In the metapelitic profile, ∆33S values from the country rocks show only a weak positive correlation with distance from the igneous contact while S isotope compositions within the Platreef are consistent with mass-dependent S isotope compositions (∆33S ≤ 0.2 ‰). Both features suggest little magma-wall rock interaction. In the metacarbonate profile, however, ∆33S values in both the country rock and the Platreef define a classic advective-dispersive tracer geometry. This geometry is not present in the associated δ34S values, revealing their susceptibility to post-transport alteration. Displacement of the ∆33S front suggests fluid advection into the country rocks; this was accompanied by back-diffusion of S isotope species into the Platreef. Counterintuitively, then, mineralization may have occurred as a by-product of fluid transport out of the Platreef ore-forming zone.
The presence of excess $^3$He, which cannot result from air contamination, is strong evidence that indigenous noble gases exist in Stardust samples. The $^3$He/$^4$He ratio can in principle fall between the protosolar and solar D-burning values. $^3$He/$^4$He is ~3.6 x 10$^{-4}$ in the sun after deuterium burning (Mahaffy et al., 1998) likely reflects the protosolar value. $^3$He/$^4$He is ~3.6 x 10$^{-4}$ in the sun after deuterium burning (Geiss et al., 2004), and 4.82 x 10$^{-4}$ in the solar wind (Heber et al., 2007). Our preliminary measured ratio of $^3$He/$^4$He falls between the protosolar and solar D-burning values.

Production of the excess $^3$He by galactic cosmic ray (GCR) spallation reactions is unlikely. While measured $^3$He contents are small (< 600,000 atoms), abundances/gram are not; the minimum grain concentration is estimated to be ~6 x 10$^5$ cm$^3$STP/g. GCR production rates in a feldspar/enstatite particle, on the Wild-2 surface or buried under 1 m of ice, are ~7-5 x 10$^9$ cm$^3$STP/g per Ma, requiring GCR exposures of ~1000 Ma, in either location, to generate only 10% of the $^3$He concentration. Estimated mass loss from Wild-2 just since its 1974 appearance is ~1 m (Brownlee et al., 2004), and was probably significantly more in the Wild-2 jet sources if they were active on previous apparitions. The collected particles were therefore likely buried until very recently at depths where GCR production is essentially nil. While ancient surfaces may be preserved on Wild-2 (Brownlee et al., 2004), only ~50% of the observed $^3$He could be produced in them by GCR spallation over the 4500 Ma age of the solar system.

References

The dynamic Archean Earth
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Archean cratons stand distinct from younger orogens as a result of their refractory lithospheric keels and relatively abundant komatiite and tonalite-trondhjemite-granodiorite (TTG) rock types. Yet detailed petrogenetic and structural studies within well constrained geochemical frameworks point to the operation of plate-tectonic-like processes as far back as 3.8 Ga. Modern geodynamic settings provide a template for interpretation of igneous rock sequences based on the assumption that melt compositions are governed by mantle mineral assemblages, dependent on depth and temperature, mediated by fluid fluxes. Application of the modern template to the Phanerozoic and Precambrian record has been validated through consideration of multiple characteristics including depositional setting, and timing and duration of magmatic and structural events. The Superior Province of North America records the formation of several independent protocontinental fragments between 3.8 and 2.8 Ga. Continental margin rift sequences suggest plume-driven magmatism, which was followed by production of plateau-type juvenile basaltic crust in the early Neoarchean. Consumption of oceanic domains of undetermined extent is recorded in <2750 Ma oceanic and continental arcs with subduction signatures including pre-orogenic boninite, calc-alkaline basalt and adakite, and syn-to post-orogenic shoshonite and sanukitoids. Five discrete collision events between 2720 and 2680 Ma united the oceanic and diverse protocontinental terranes. Evidence from the western Pilbara craton supports the operation of subduction by 3.12 Ga, whereas the 3.51-3.24 Ga sequences of the eastern Pilbara appear to have evolved in a plume setting (Smithies et al. 2005). However, evidence for even earlier sea-floor spreading within a plate-tectonic framework derives from the 3.8 Ga Isua belt (Furnes et al. 2007). It is likely that plumes were a common heat-release phenomenon early in Earth history, and once may have been dominant, but evidence for Neoarchean plume-arc interaction (Dostal and Mueller 1997) suggests that as in the modern Earth, plumes were not incompatible with organized convection. Evidence from the Hadean record is scant and views of Earth’s very early evolution are guided by thermal models and insights from planetary geology.

Many features of Archean terranes appear to be directly (komatiites, charnockites) or indirectly related to higher mantle temperatures. The highly depleted compositions of lithosphere keels may result from fluxed melting of depleted mantle in high-temperature suprasubduction-zone wedges.

References
TEM evidence for lead transport by bacteria in atmospheric deposition

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Particulate matter (PM < 5) present in atmospheric deposition and subsurface soil water has been monitored during one year in two different, polluted and non polluted environments located in France. One site is a vineyard and the other one is a forest considered as an unpolluted reference site. Coupling TEM and EDX permits single-particle characterization (composition, structure, size and morphology).

PM in rainfall, leachate and soil solution show similar characteristics for both sampling sites: among more than 10000 characterized particles, 10 to 20% of the relative surface area is of biological type. Different morphotypes of bacteria and associated amorphous organic matter are regularly and significantly concentrated in lead. Lead is always associated with phosphor forming one or several granules confined inside the bacteria cell (Figure 1).

![Figure 1. a) Bacteria with internal granules (arrow). b) EDX spectrum corresponding to arrow in figure 1.a.](image)

Such lead enrichments inside internal granules have been previously shown (Roane, 1999; Suh et al., 1999) in laboratory experiments. Our study proves for the first time such an occurrence in natural environments. The presence of bacteria in both rain water and soil water suggest an ubiquitous behaviour of microorganisms and an atmospheric origin for the lead. Even if the source of lead is not known, our result furnishes evidence for a microbial airborne lead transport.

References

Estimating geochemical impacts of uranium mining exploitation: The evaluation of the natural background in the Beiras metallogenetic province (Central Portugal)


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The evaluation of the geochemical and radiological impacts associated with uranium mining activities requires a comparison, for each environmental compartment, of data taken before and after the end of mining works. With a few exceptions, no environmental data is known for Portuguese old uranium mines regarding the natural background before exploitation. A possible way to overtake this limitation is to obtain data from areas which constitute a natural analog of those that were mined for uranium ores, but where exploitation did not occur. The Oliveira do Hospital area, located in Central Portugal, fulfills such requirements; here, late-tectonic Hercynian granites and pre-ordovician metasedimentary rocks dominate. 24 samples of surficial and groundwaters were collected in the region, as well as 14 samples of soil and 5 of stream sediments. These samples were analysed for more than 40 chemical elements, using several analytical techniques. The results obtained allowed to establish reference values for the geochemical background, taking into consideration central tendency and variability parameters. An important conclusion is that several elements are frequently concentrated by natural processes above the limits referred in the literature and/or legislation as indicating anthropogenic contamination (e.g. Ba, As, P and Be in soils, $^{226}$Ra in waters), which reinforces the interest of the evaluation of the local geochemical background, as an alternative to the use of global reference values.
Hydrogeochemistry of water resources from abandoned Freixeda gold mine (NE Portugal)

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Freixeda mine is located in NE Portugal and was exploited for Au, Ag and Pb. It belongs to the Auriferous Methalogenic Province of NW of Iberian Peninsula. The mineralization is associated with sulphide minerals in quartz veins, located in metasedimentary paleozoic formations.

Water samples were collected from a gallery with acid mine drainage (AMD), 3.5 < pH < 4.0, and from groundwater and surface water, upstream and downstream from the mine influence. Water from Ribeira de Freixeda upstream from the AMD confluence is not affected by the mineralization and has Ca-HCO₃ type, slightly basic pH with no detectable As and no significant concentration of trace metals. Downstream from the AMD, surface water becomes Ca-Mg-SO₄ type with elevated concentrations of As, Zn and Mn.

Groundwater from a spring outside the influence of the mine has a pH of 6.5 and is of Ca-Na-HCO₃ type with no anomalous trace element concentrations. Groundwater exploited from a deeper well is of Mg-SO₄ type, pH about 7 and has high concentrations of As, Zn, Mn and Fe.

Conclusions from this study are that water resources of Freixeda are affected by sulphide mineral oxidation which releases cations, SO₄²⁻ and H⁺ ions. These free H⁺ ions contribute to the dissolution of carbonates (present in cement of metasedimentary rocks) and to the hydrolysis of silicate minerals (plagioclases) promoting the alkalinity and pH increase.

Concentration of As in surface water is much lower than in groundwater probably do to adsorption of As on Fe oxyhydroxides, that precipitates in stream sediments. This suggestion is supported by the absence of dissolved iron in surface-water samples. Even so, the amount of As (190 ppb) in surface water is above the limit for human consumption or watering. In groundwater, the oxidation-reduction potential and pH conditions that allow Fe to remain in solution could be responsible for the higher concentration of As (850 ppb).

Introduction to the CAMECA IMS 7f-GEO

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SIMS is applied to a variety of applications in Geoscience, because it offers sensitivity compatible with very local isotopic and/or elemental analysis of solid samples.

Large SIMS instrument like the CAMECA IMS 1280 offers outstanding performance for the entire SIMS application range (dating experiments, stable isotopes, REE analysis) thanks to its very high transmission mass spectrometer combined to a versatile multi-collection system. However, sometimes this tool can be seen as oversized for a laboratory with a limited application range. Therefore CAMECA has introduced the IMS 7f-GEO, a compact SIMS model with new features targeted to improve performance for isotopes and trace element analysis:
- Quasi-continuous record of the primary ion current during analysis.
- Magnetic sector with a very fast peak switching capability over the full mass range (magnetic and electrostatic peak switching combination).
- Secondary ion detection equipped with an EM and a pair of Faraday cups. Double FCs configuration makes possible to run an analysis in a pseudo-bicollection mode well-suited for stable isotope analysis.
- High precision Faraday Cup electrometer.

Typical analytical performance of the IMS 7f-GEO for stable isotope analysis (¹⁸O/¹⁶O): for an analysis area of 10x10µm², a single analysis internal error of less of 0.3 per mil is reached for a total integration time < 60sec. Detailed instrumental features and experimental data will be presented.
Heavy metals content in Belgrade soils

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The main goal of the paper is to present results of researches held from 2004 to 2006 regarding heavy elements content in the Belgrade city soils. Lot of 153 soil samples from 24 different locations were taken and analyzed from 2004 to 2006 in laboratory "MOL" (Belgrade).

Methods

Samples were taken from exact localities, from the topsoil (surface soil) – 0-15 or 0-20 cm of depth. Each sample was prepared as a composite of few sub-samples using standard techniques (EPA method 3040).

Different instrumental methods were used to determine concentrations of desired elements: (EPA 213.2), (EPA 206.2), (EPA 249.1), (EPA 220.1), (EPA 218.1), (EPA 289.1) and (EPA 245.1); spectrophotometric technique was used for determining chromium concentrations.

Discussion of results

<table>
<thead>
<tr>
<th>Min conc. (ppm)</th>
<th>Max conc. (ppm)</th>
<th>MAC* (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb 1.22</td>
<td>792</td>
<td>100</td>
</tr>
<tr>
<td>Cd 0.02</td>
<td>36</td>
<td>3</td>
</tr>
<tr>
<td>Hg 0.1</td>
<td>18</td>
<td>2</td>
</tr>
<tr>
<td>As 0.2</td>
<td>85</td>
<td>25</td>
</tr>
<tr>
<td>Ni 0.60</td>
<td>224</td>
<td>50</td>
</tr>
<tr>
<td>Cr 5</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td>Zn 1.01</td>
<td>3375</td>
<td>300</td>
</tr>
</tbody>
</table>

* according to Serbian instructions on Soil Quality

On the most of the localities (21 out of 24) certain excess of concentration of elements, which are important for soil pollution assessment, is determined. Only in a single case exceeding concentration of chromium was related to geological factors; in other 152 out of 153 cases – human activities were only source of pollution. Nickel concentration in soil samples from Belgrade area exceeds MAC of 50 ppm in 20 of 24 samples. Concentration reaches up to 228 ppm in soils from New Belgrade.

On the localities of Ada Ciganlija excess in concentrations for six elements and in New Belgrade of four elements were determined. Samples of river mud from Ada Ciganlija lakeshore showed very high level of contamination with lead, nickel, copper and especially zinc.

References


Low water contents in minerals from Gakkel ridge abyssal peridotites, Arctic Ocean

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We report the first water contents ever measured in abyssal peridotite minerals. The analyses are made possible by the exceptionally fresh state of a few Gakkel Ridge peridotites that show almost no serpentinization. Gakkel ridge is the slowest spreading ridge on Earth (Michael et al., 2003). The three preliminary samples analyzed so far come from dredge haul PS66-238 (Snow et al., 2007) from an amagmatic region where no basalts were found, and the extent of melting is low to none. FTIR spectra of olivines and pyroxenes resemble previously published ones (e.g., Miller et al., 1987, Skogby et al., 1990). Water contents in one peridotite correlate with grain size in olivines and are variable in orthopyroxenes, whereas those of the two other samples are homogeneous. No water variations are observed within individual grains.

Calculated water concentrations in H2O ppm are < 1-5 for forsterities, 25-60 for enstatites, and 130-200 for diopsides. These water contents are 2 to 3 times lower than typically found in continental spinel and garnet peridotites (e.g., Peslier et al., 2002; Peslier and Woodland, 2006). Recalculated whole-rock water contents of the abyssal peridotites are, at most, 50 ppm, about half the amount calculated from MORB-glass analyses for the depleted-MORB mantle (DMM) (e.g., Dixon et al., 2002). The low water contents of the abyssal peridotites also contrast with water contents measured in MORB glasses from Gakkel Ridge which are higher than those of MORB globally (Michael et al., 2006). If the low water content of Gakkel ridge abyssal peridotites is representative of that of the Earth's oceanic mantle, models for extents of melting, major and trace element trends and crustal thickness at mid-oceanic ridges (e.g., Asimow and Langmuir, 2003) need reassessment.

References

The chemistry of diffuse-flow vent fluids on the Galapagos Rift (86°W): Temporal variability and subseafloor phase equilibria controls

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Recent (2002, 2005) expeditions to the Galapagos Rift, 86°W have conducted integrated experiments to assess temporal/spatial changes in both the chemistry and associated biology of diffuse-flow hydrothermal vents. The chemical data adds significantly to time series observations of hydrothermal processes at the Galapagos Spreading Center (GSC), where seafloor venting was first discovered in 1977. Assuming quartz-fluid equilibria (0.55 NaCl solution), end-member values for dissolved silica in 2002/2005 indicate temperatures ~50-100°C lower than in 1977. The higher predicted temperature in 1977 is consistent with observed chlorine depletion in fluids issuing from Oyster Beds vent, indicating fluid phase separation, whereas all fluid samples from 2002/2005 are at or above seawater concentration. Respective values of dissolved Mn further suggest a lower temperature hydrothermal reaction zone at 86°W relative to three decades ago. The slope of Li-Si data from 1977, however, does not depart significantly from the 2002/2005 data, suggesting temperature change has little effect on dissolved Li in the hydrothermal endmember. At some point between 1990 and 2002 a volcanic eruption covered the historical Rose Garden vent-field, ending years of biological observations. Although the precise age of the lava flow is uncertain, the lack of chloride depletion and low H2S/heat ratios of the 2002/2005 vent fluids suggest the 2002 expedition arrived well after the eruption based on observations from other diffuse-flow systems perturbed by volcanic activity. Lower dissolved silica, Mn and H2S in the 2005 vent fluids relative to 2002, however, may indicate continued cooling in the aftermath of the recent eruption. Results of geochemical modeling for evolved seawater in equilibrium with a moderately oxidizing mineral assemblage are consistent with chemistry of recent GSC fluid samples, predicting H2S/Fe > 1, with little Fe in fluids diluted to the extent typical of 86°W vents. Results from in-situ chemical sensor measurements reveal non-conservative behavior of dissolved H2S, especially at temperatures below 10°C, which may be due to microbial metabolism.

Quantification of sulphur cycling at the Mid-Atlantic Ridge

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Mid-ocean ridges and associated hydrothermal vent systems represent a unique scenario in which the interaction of hydrosphere, lithosphere and biosphere and the related element cycling can be studied. Here, we present concentration and isotope data (S, O, H, C) for hydrothermal fluids and their dissolved constituents as well as from mineral precipitates collected at the Logatchev hydrothermal field (14°45′N) and different sites at the southern MAR (4° – 11°S).

δ34S values for dissolved sulphide and metal sulphides from the emanating hot fluid itself or pieces from black smokers between +1.9 and +8.8‰ (V-CDT) suggest that sulfur represents a mixture between mantle sulfur and reduced seawater sulphate. More detailed quantifications are based on the rare sulfur isotopes (33S and 36S) suggesting a contribution from recycled seawater sulphate between 20 and 30%.

Dissolved inorganic carbon in hydrothermal fluids from both hydrothermal areas show characteristic δ13C values around -3.9‰ (V-PDB, end member corrected).

Isotope values of Δ18O = 2.2‰ and Δ2H = 6.6‰ for the hydrothermal fluids at Logatchev and southern MAR sites clearly point to intense interaction between fluid and host rock. Very high sulphide concentrations up to 8.2mmol/L (calculated end member) measured for fluids from the Turtle Pits site (5°S) indicate an early stage of hydrothermal activity and are consistent with young volcanism. This indication is supported by very high fluid temperatures up to 407°C for the black smoker “Two Boats”.

Strongly negative sulphur isotope values as low as -24.0‰ for sulphidic sediments at the Logatchev HF are clear indicators for bacterial activity and, thus, point to the participation of microbial communities in sulphur cycling at the Mid-Atlantic Ridge.

The results, so far, provide a deeper insight into element cycling at the Mid-Atlantic Ridge, including apparent differences to fast-spreading ridge systems, such as the East-Pacific Rise (EPR).

Acknowledgements

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Sequential extraction of radioactive metals in soils from Crucea uranium mine (Romania)

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ICP and XRF Spectroscopy methods were used to evaluate the metals (ppm) from soils for the mining dumps of Crucea-Botusana uranium deposit (Bistrita Mountains, Romania).

The sequential extraction has emphasized the fact that U is associated with all the mineral fractions present in the soil samples. A great percentage of U can be found in the carbonate, organic and oxides fractions. The percentage of U detected in the exchangeable fraction is rather small. The fact that 21.77% of the total U can be found in the specifically absorbed and carbonate bound fraction, indicated the important role played by the carbonates in the retention of U; on the other hand this fraction is liable to release U if the pH should happen to change.

Th appear in high-enough concentration in the soil is scarcely available because 70.29% is present in residual fraction, and about 21.78% in the organic and oxides fractions. This is certainly due to the fact that this naturally occurring radionuclide can be associated with relatively insoluble mineral phases like alumino-silicates and refractory oxides. Its association with the organic matter suggests that it can form soluble organic complexes that can facilitate its removal by the stream waters.

In the case of Sr, the sequential extraction shows that it is very strongly fixed because the residual fraction concentrates the great amount of this element. What is interesting is the percentage of 2.65 % of Sr from the exchangeable fraction because it can be easily released and transported to the surrounding environment.

Pb it is present in various relatively soluble pools (17.81% in carbonate bond and 34.85% in organically bound), which appears to be an efficient sink for this element. This fact may indicate a possible link between the biological activity and the Pb cycling into the soil. In addition, only 17.78% is present in the insoluble residual fraction.

Although from our research it resulted that the radioactive metals does not concentrate in the exchangeable fraction (Th) or it concentrates very little in it (U and Sr), the isolation of the mineral fraction of soil rich in U, Th and Sr helps us in the future identification of the connections which control the cycle of the radioactive metals.

These results have important implications for remediation strategies. The thorium and uranium from Crucea mining area are in labile, not strongly retained, fractions, thus making them amendable for remediation by phytoremediation.

Phase decomposition in non-isotropic multi-component systems: The alkali feldspar example

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Phase decomposition in a multicomponent system is considered theoretically. The approach of non-linear diffusion is used and the corresponding system of Cahn-Hilliard equations is systematically derived from the expansion of the free energy. In contrast to the standard Cahn-Hilliard model the possible anisotropy of the system is taken into account. The final equations set is solved numerically using a finite element approach. Realistic approximations for the free energy are used. The numerical solutions are finally compared to observations made on naturally exsolved feldspar. Good qualitative agreement is found. The morphology of exsolution phases depends on the composition of the homogeneous precursor feldspar and on the degree of anisotropy. Host-inclusion arrangements are obtained, when the bulk composition is close to one of the spinodal points and a co-continuous morphology is obtained, if the bulk composition is half way between the respective binodal compositions. For feldspar compositions that lie close to the albite-K-feldspar binary, the anorthite component is preferentially fractionated into the albite-rich exsolutions.
Isotope-geochemical criterion in search for the Noril’sk-type massive PGE-Cu-Ni sulphide ores: Constraints from Pb, Nd and Sr isotope data

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Our study aims on isotope-geochemical speciation of main types of intrusive bodies at Noril’sk district (northern Siberia), with particular focus on isotope-geochemical estimation for the unique metallogenic potential of the Noril’sk-type intrusions that range in thickness to 360 m and length to 25 km.

This study presents the first results of a multi-technique approach, which utilized isotope systematics of Nd, Sr and Pb for rock-forming minerals (i.e. pyroxene, plagioclase and olivine) and associated sulphide minerals (disséminated ores) derived from main lithological units of various ultramafic-mafic intrusions (namely economic Noril’sk-1, Talnakh and Kharaelakh, subeconomic Zub-Marksheider and Vologochan, prospective Mikchangda and none-economic Nizhny Talnakh). Initial Sr and Pb isotope ratios have been also determined in massive sulphide ore samples at Talnakh and Kharaelakh.

Initial Sr and Pb isotope compositions of plagioclase and sulphide (67 analyses) significantly differ from each other indicating their isotope heterogeneity. Similarly, contrasting difference in the Sr isotope composition has been observed for the rock-forming silicate minerals and sulphide ores. At Talnakh and Kharaelakh, concentration of Sr in massive sulphide ore varies from 4 to 30 ppm; (87Sr/86Sr)0 varies in the range 0.7085-0.7111, whereas in plagioclase and pyroxene (87Sr/86Sr)0 usually not exceeds 0.7076. This implies that sulphide ore melt appeared in its location site as isotopically heterogeneous mechanical admixture, marked by specific isotopic compositions of Pb and Sr, different from that of rock-forming minerals. It is noteworthy that sulphide ores, in comparison with silicate minerals, were essentially enriched by radiogenic Sr component at time of intrusion.

In Sr-Nd isotope systematics silicate matter from economic ore-bearing intrusions (about 60 bulk rock samples, plagioclase and pyroxene extracted from the bulk rocks) in comparison with silicates from none-economic weakly mineralised intrusions (81 sample) manifest clear contamination by the component, which along with relatively constant the Nd isotope composition (epsilon Nd about +1±0.5) is enriched with the radiogenic Sr. This feature can be employed as a prospective sign for the presence of significant quantities of the ore contaminant, which has isotope signatures close to that of massive sulphide ores.

Quantifying mineral aerosol inputs and the mobility of “immobile” elements in weathering studies

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Calculations of chemical weathering fluxes rely on a complete characterization of the mass balance for a given system. This study addresses two issues that may play an important role in these calculations. The first issue is that of mineral aerosol inputs, which can be a significant contribution to the overall atmospheric flux. Appropriate spatially and temporally averaged values for mineral aerosol fluxes are not easily established. The second issue is the use of “immobile” index elements such as Ti and Zr in the calculation of weathering losses of other elements. This study focuses on an analysis of mineral aerosol inputs and mobility of a wide variety of trace elements from the Rio Icacos watershed in the Luquillo Mountains of Puerto Rico. Additionally, this study puts the findings from the Rio Icacos in a global context based on literature review.

Results of our analyses in the Rio Icacos illustrate that Sr isotopes may be used to calculate watershed-scale average mineral aerosol deposition fluxes given a situation of a monolithologic catchment, a difference in the 87Sr/86Sr ratio between the bedrock and the mineral aerosol inputs, and Sr-bearing primary minerals weathering to completion in the regolith. Nd isotopes are used to demonstrate that mineral aerosol inputs are incorporated to a depth of >3 meters in the regolith.

Trace element and rare earth element data were analyzed in order to assess patterns on elemental mobility within Rio Icacos regolith. Of all elements, Zr indicates the least mobility in this system, yet Zr data indicate leaching losses of ~50%. Alternatively, the saprolite has expanded by a factor of 2x during formation, but volume expansion is considered highly unlikely based on textural evidence. Calculations of mass losses during chemical weathering based on normalization to trace elements therefore require careful consideration in the case of intense weathering environments.
Interaction of the hydrologic cycle with the continental crust exerts a strong influence on the chemical composition of the ocean and atmosphere. Advanced models of long-term ocean/atmosphere evolution therefore critically depend on reconstructions of the hydrologic cycle and bedrock geology in the geologic past.

Here, I argue that important aspects of past surface geology can be reconstructed from radiogenic isotope records of seawater. These reconstructions rely on linear correlations between bedrock age and lithology with the isotope composition of continental runoff (Peucker-Ehrenbrink, submitted). Global and regional bedrock lithology and ages are quantified using GIS technology and digital geologic maps at resolutions of 100 to 10,000 square kilometers per polygon, whereas chemical characterization of runoff relies on literature compilations. Inverting the marine Sr isotope record in this fashion yields average bedrock ages of the continental drainage in the geologic past. This new paleo-age record indicates older mean bedrock ages in the early Paleozoic, bedrock rejuvenation from the Paleozoic into the Mesozoic and an aging trend that started in the Cenozoic. In general, aging corresponds to greater exposure of igneous and metamorphic rocks whereas rejuvenation is driven by greater exposures of sedimentary and/or volcanic rocks.

The general validity of this bedrock-age record can be independently tested with paleo-geologic reconstructions by Ronov and coworkers (as quantified by Bluth & Kump, 1991), as well as the Nd isotope evolution of sedimentary rocks from large-scale continental drainage regions (e.g. Patchett et al., 1999). Both are suggestive of a trend towards younger bedrock from early to late Paleozoic, broadly similar to the paleo-bedrock record.

The application of this concept to the marine Os and Hf isotope records requires investigating the relationships between river isotope chemistry and drainage basin geology (Peucker-Ehrenbrink & Miller, in press). Marine paleo-records for Nd need to be spatially averaged due to the short residence time of Nd in seawater and the large isotope variability in continental Nd sources (e.g., Jeandel et al., 2007); alternatively, they may yield insights into regional changes in continental drainage geology in the geologic past.

References

The 1.16 Ga Ilímaussaq intrusion is part of the Proterozoic Gardar Province, S Greenland, and type locality of agpaitic rocks. The latest of these agpaites crystallized from floor to center of the magma chamber and involve bottom kakortokites and central lujavrites (Sørensen et al., 2006). Similar in terms of chemistry and mineralogy, kakortokites and lujavrites are distinguished texturally. Kakortokite is strongly laminated, subdivided in 29 layered units, each of which consists of a three-layer sandwich (a lower arfvedsonite-rich black layer, a central red eudialyte-rich layer and an uppermost white layer rich in nepheline and feldspar). Lujavrites are divided into two main groups (green and black), depending on the prevalence of aegirine or arfvedsonite, respectively. Aegirine lujavrites are further divided into two textural varieties (I and II), where aegirine lujavrite II is more fine-grained and lamination and fissility are not as extreme as in aegirine lujavrite I.

Kakortokites and lujavrites were investigated by microscopy, electron microprobe and LA-ICP-MS. We present crystallisation sequences, main and trace element variations and distribution coefficients between eudialyte, amphibole and pyroxene. The mineral chemistry of amphibole and eudialyte reveals a continuous evolution within this series in terms of increasing Mn/Fe and decreasing Ca/REE ratios, whereas whole rock chemistry remains almost constant. Evolutionary trends are hardly recognized in the lower kakortokite sequence, but very well in the upper kakotokites and lujavrites. Central vertical profiles show significant element variations, which are not observed in marginal or horizontal profiles.

Magmatic assemblages are partly altered by post-magmatic hydrothermal fluids. In accordance with results from Pilanesberg, South Africa (Mitchell and Lifervich, 2006), five different alteration stages are observed, which are related to fluid pH variations. Interestingly, the assemblages alternate between agpatic and masikitic. Alteration starts with the breakdown of eudialyte and the formation of a masikitic mineral assemblage of mainly katapleiite, britholite and analcime. After the breakdown of nepheline, the Na/Cl ratio (and hence, pH) increases and an agpatic mineral assemblage including sodalite and analcime is stable again. Subsequently, a masikitic albization and formation of nepheline II follows leading to a drop in the Na/Cl ratio. Finally, the last stage is represented by the reaction of amphibole to pyroxene and biotite and the formation of cancrinite.

References
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High-field strength elements (Nb, Ta, Zr, Hf) in continental basalts from the CEVP – Implications for the HFSE budget of the lithospheric mantle and the global Nb budget

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Nb/Ta ratios in continental basalts from the Central European Volcanic Province (CEVP) are among the highest values measured so far in terrestrial rocks by high-precision methods. In volcanic rocks from the Rhön, Vogelsberg and Eifel regions, Nb/Ta ratios are subchondritic (<19.9) with values between 15.0 and 19.1 and on average higher than in ocean island basalts at comparable Zr/Hf ratios (see figure). This observation is investigated within the context of a potentially Nb enriched lithospheric mantle that may play a role in balancing the global Nb budget.

Crustal contamination of most samples is displayed by elevated 187Os/188Os ratios (~0.150), but samples having low (i.e. mantle like) 187Os/188Os (~0.129-0.150) have the highest Nb/Ta ratios, indicating that the elevated Nb/Ta ratios are not imprinted by crustal assimilation.

Nb/Ta ratios are positively correlated with Lu/Hf ratios in all but the Vogelsberg tholeiites, a feature that cannot be explained by partial melting of either spinel or garnet peridotite sources, but by the mixing of asthenospheric melts from a garnet bearing source with melts produced from amphibolitic veins. High HFSE concentrations and elevated Nb/Ta ratios (~17) with respect to the asthenospheric mantle (~14) require only low amounts of such melts in the order of a few percent. Therefore, elevated Nb/Ta ratios within some of the volcanic rocks of the CEVP do not mirror elevated Nb/Ta ratios within the subcontinental lithosphere itself, but reflect the presence of HFSE enriched, amphibole rich domains from which high Nb/Ta melts are produced during magma ascent and remelting.
Studies for the sorption of metals from lake water using limestone and rice bran

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Environmental research studies were carried on Noor Mohamed Lake in Katedan Industrial Development Area Hyderabad, India. The study reveals that the lake was highly contaminated with industrial effluents. Contamination of lake was due to release of industrial effluent containing organic and inorganic chemicals. A sorption experiment using laboratory columns was carried on lake water to reduce the concentration of heavy metals to limited extent, in this study an agricultural by product rice bran (30%) and a geological media limestone (70%) has been successfully used for reducing the concentration of metals in lake water. The Medias are efficient in reducing metal concentration by Sorption, adsorption, precipitation, oxidization and reduction reactions involved in process which depends on the factors like pH, surface areas of reactive media and porosity.

Vertical columns open at both the ends made of polyvinyl chloride of length 50 cm / 10 cm diameter was packed with two different medias in 3:7 ratio covered with a filter paper and closed with Teflon lids fitted with Silicon tubes of 3 mm size and effluent was passed using a peristaltic pump with speed of 55 rpm / 10 ml per minute. The experiment was carried for one week and the sample was collected from outlet, analysed for pH, E.C, TDS and metals like Zn, Cu, Cr, Pb, Ni by inductively coupled plasma optical emission spectrometry (ICP-OES).

The results shows that there was no change in pH but a slight increase in total dissolvable solids from 1026 ppm to 1857 ppm, this was due to the release of dissolvable solids from the medias, concentration of metals for Cr-43.52ppb (Cr-68% removal), Zn - 98.25ppb (Zn-88% removal), Cu–30.43ppb (Cu-41% removal), Ni–27.44ppb (Ni51% removal), Pb–15.62 ppb (Pb-84% removal) with limestone and rice bran.

References

Contribution of two main smelters on urban soils pollution in northern France investigated by lead isotopes

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Introduction and objectives
The studied urban zones are located in northern France at the vicinity of two base metal smelters which are 3.5 km distant from each other. Historical Pb, Cd and Zn contamination through atmospheric emissions from both plants has been demonstrated by different authors (Frangi et al., (1997) or Sterckeman et al., (2002) on cultivated soils).

Urban (kitchen garden and lawn) soils in the studied zones present varying and sometimes higher Pb contents than the neighbouring cultivated soils (Pruvot et al., 2006). Pb isotopes have then been used to better constrain the contribution of each emitter to the observed pollution. A second aim was to look for other possible sources of contamination (manures with ashes or slag, other atmospheric inputs…) to explain the anomalous contents.

Analyses have been performed on homogenised samples from the upper 25 cm of the garden soils. Pb isotopic compositions were analysed by TIMS on a MAT-261. Pb, Cd and Zn concentrations were obtained by GFAAS.

Isotopic results and discussion
Garden soils with different lead contents and supposedly various cultural practices show a distribution into two distinct and homogeneous lead isotopic signatures. Each signature corresponds to soils located in the vicinity of one of the two plants. This supports the hypothesis of a quite exclusively airborne pollution related to one refinery activity. Furthermore, mixing of the two lead types can be observed on one soil located in between the two refineries, which displays an intermediate isotopic composition. Additionally, whatever its chemical speciation, lead obtained by single chemical extractions performed on some garden soils shows isotopic homogeneity within a specific soil, suggesting that pollution has affected all soil compartments.

References
Elemental-sulfur reducing or disproportionating organisms in a ~3.5 Myr-old seafloor setting

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We report multiple-isotope sulfur analyses ($\delta^{34}S$, $\Delta^{33}S$) of sulfides and sulfates from a unique collection of pristine drill core samples (Pilbara Drilling Project; Van Kranendonk et al., 2006) from the 3,490 Myr old Dresser Formation at North Pole, Western Australia. We show that the strongly $^{34}S$-depleted microscopic sulfides preserved in barite crystals that have been interpreted as evidence for sulfate-reducing organisms during the early Archean (Shen et al., 2001; Shen and Buick, 2004) have mass independently-fractionated sulfur isotopic anomalies ($\Delta^{33}S$) different from their host barite and therefore that they cannot have been produced by sulfate reducing microbes. Instead, we interpret the combined negative $\delta^{34}S$ and positive $\Delta^{33}S$ signature of these microscopic sulfides as evidence for the early existence of organisms or consortia that reduce or disproportionate elemental sulfur. These results support the prediction arising from phylogenetic reconstruction that elemental sulfur reduction is among most deeply-rooted metabolic pathway in both of the prokaryotic Domains.

References

Supercontinental warming, plumes, and mantle evolution

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Large-scale magmatism is often linked to the breakup of a supercontinent, but it is not established whether it is caused by a plume head or a global temperature increase of the mantle. On the basis of convection modeling in an internally heated mantle, we have shown that continental aggregation promotes large-scale melting without requiring the involvement of plumes (Coltice et al., 2007). When only internal heat sources in the mantle are considered, the formation of a supercontinent causes the enlargement of the wavelength of the flow and subcontinental warming as large as 100 °C. We will show how plumes interact with supercontinental warming in order to better understand the evolution of melting during the opening of Pangea.

We will also describe the importance of the supercontinental warming model over the course of the evolution of the Earth’s mantle and the growth of the continental crust.
In-situ cosmogenic nuclides are widely and increasingly used for to study earth-surface processes and its recent history, but these goals have been impared by inconsistencies in the understanding of the production systematics. The CRONUS-Earth Project was funded by the U.S. National Science Foundation with the objective of reconciling these discrepancies and providing a generally accepted basis for interpreting cosmogenic nuclide data. The Project is approximately half-way through its five-year duration and has achieved significant progress toward these goals. Areas of considerable uncertainty that have seen major advances include samples for $^{36}$Cl production-rate calibration and spatial/temporal scaling of production. New paleomagnetic reconstructions have become available to complement improved scaling theory, resulting in testable predictions of global production patterns. The relation between geologically-based and neutron-monitor based scaling has been elucidated through monitoring of neutron-monitor-response physics. Calibration samples have been collected in a rigorous fashion from sites associated with the shoreline of Lake Bonneville, Younger Dryas glacial sites in Scotland, and LGM glacial sites in the Puget Lowland of Washington State, a locality of particular importance for resolving discrepancies in $^{36}$Cl production. Essential data and tools include improved production cross sections from neutron beam experiments and the release of a web-based cosmogenic calculator for the community.

### Extraction of biosignatures from weathered basalts

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There is a growing interest in the bio-load in weathered volcanic rocks. The relevance extends to Mars, where there are extensive regions of weathered basalt. Any bio-load in such rocks is likely to be very low, so it is essential to maximize the extraction efficiency for analysis. Analysis of suites of regolithic Tertiary (~60 Ma) basalt from Skye, Scotland, show the importance of particle size for optimal organic recovery.

Basalt from two localities was divided into fine (<500µm)- and coarse (>1cm)-grained fractions and surface contamination removed using acetone. They were then crushed and sieved into five different grain size fractions and subsequently soxhlet-extracted for 48 hours with 93:7 DCM/methanol.

The data show that a reduction in grain size results in a higher yield of extractable organic material (EOM) (Table 1). The n-alkane odd-over-even preference (OEP) exhibited by the GC-MS trace (Fig. 1) indicates that the extract is thermally immature, consistent with a recent biological (microbial) signature.

#### Table 1: EOM (%) for different grain size fractions.

<table>
<thead>
<tr>
<th>Glen Varradale basalt</th>
<th>Quiraing basalt</th>
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<tr>
<td></td>
<td>CG&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>&gt;425µm</td>
<td>0.001</td>
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<tr>
<td>425-125µm</td>
<td>0.001</td>
</tr>
<tr>
<td>125-63µm</td>
<td>0.002</td>
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<tr>
<td>63-38µm</td>
<td>0.002</td>
</tr>
<tr>
<td>&lt;38µm</td>
<td>0.003</td>
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<sup>a</sup> Coarse-grained; <sup>b</sup> Fine-grained

#### Figure 1: GC-MS trace of the saturate fraction m/z 85 ion from the Quiraing basalt. Note marked OEP of n-alkane peaks.

The data emphasise the importance of analysing a fine grain size during processing of samples, including future Mars missions, where volcanic rocks may be targeted.
Role of bacteria on uranium migration in a calcareous peatland

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The assessment of a polluted site is usually undertaken through its hydrogeochemical characterization and the impact of the implied conditions on pollution migration. However, in specific natural environments, such as peatlands, microbial activity can also affect, directly or indirectly, this migration.

A calcareous peatland polluted with uranium particles (about 3.5 ppb) contained high concentrations of total dissolved uranium from the surface to 0.8 m deep (up to $7 \times 10^{-6}$ mol.L$^{-1}$). This can be explained by the formation of the major complex Ca$_2$UO$_2$(CO$_3$)$_3$. Even though uranium particles have also been found between 0.8 and 2 m, total dissolved uranium concentrations are very low ($1 \times 10^{-10}$ mol.L$^{-1}$). At these latter depths, where the peat remains humid (water – table from 0.25 to 0.8 m), uranium solubility can decrease due to reducing conditions. The increasing occurrences of framboidal pyrite particles at depths lower than 0.8 m suggest reducing conditions related to sulfate – reducing bacteria.

In order to study the impact of these bacteria on the physico – chemical conditions of the peat soil, batch experiments were performed. Using various types of carbon sources (ethanol, oxalate) and doping with sulfate, trimethylphosphate and uranium, at 25 °C and 5 °C, the total dissolved uranium content was followed throughout the incubation. The ethanol – doped batch incubated at 25 °C shows a significant decrease of uranium from $1.95 \times 10^{-5}$ to $3.93 \times 10^{-8}$ mol.L$^{-1}$ in 200 hours. Other parameters (pH, Eh, dissolved oxygen, [SO$_4^{2-}$], [HS$^-$], etc.) are also followed and compared to the equation of microbially – mediated sulfate reduction:

$$2\text{CH}_3\text{O} + \text{SO}_4^{2-} \leftrightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}$$

These batch experiments and the identification of the bacterial populations (via 16S rDNA sequence) show that sulfate – reducers in peatlands produce reducing conditions that can immobilize uranium and possibly other trace metals.

References
Seismic anti-correlation in the mantle: Is hot blue and cold invisible?

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Low levels of bulk sound velocity ($V\Phi$) variations below 2000 km depth in the mantle and a prominent anti-correlation of $V\Phi$ to shear seismic wave velocity ($V_s$) near the core mantle boundary are typically used to infer the presence of compositional deep mantle heterogeneity. Using a thermodynamically self-consistent mantle mineralogy model based on Gibbs free energy minimization we show that these effects can arise from differences in the isothermal and adiabatic bulk modulus at high pressure and temperature of the Earth’s lower mantle, and that it is possible to reproduce the observed $V_s/V\Phi$ anti-correlation in a chemically uniform mantle. The mineralogy model provides us with elastic constants and density for any given P,T condition.

We take this density to compute convective buoyancy forces in a simple (2-D purely bottom heated isoviscous and isochemical) compressible mantle convection model. Our approach allows us to predict a number of seismic observables from the convection model, all of which agree remarkably well with observations from a tomographic study. Our results are fully compatible with other published mantle mineralogy models, which similar to our finding predict an increase of $\partial V\Phi/\partial T$ with temperature and pressure, and a pronounced $V_s/V\Phi$ anti-correlation in the lowermost mantle.

Contracting KREEP magmatism in the early evolution of the Moon

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Ages of zircons from lunar Breccias

Previous (SHRIMP) age studies of zircons from lunar granophyres and other rocks (Meyer et al. 1996) showed that zircon-forming magmatism in the lunar highlands was continuous from 4.3Ga until at least 3.88Ga. We have further investigated the distribution of lunar zircon ages by undertaking SIMS U-Pb isotopic analyses (SHRIMP II at Curtin University and CAMECA 1270 at the Swedish Museum) of zircons from breccias from the Apollo 14 and Apollo 17 landing sites.

U-Pb results

Analytical results, presented on concordia plots on Figure 1, show that Apollo 14 and 17 zircons have essentially identical age patterns in the range 4.35 to 4.20Ga, but, whereas Apollo 14 zircons have ages in the range 4.20 to 3.9 Ga, zircons from Apollo 17 samples have no ages younger than 4.20Ga.

Interpretation

Our results show that lunar zircon-forming magmatism was not continuous from 4.35 to 3.88Ga everywhere on the Moon, but has a marked regional asymmetry. We explain this by proposing that between about 4.35 and about 4.20Ga the source reservoir for zircon-forming KREEP magmatism contracted to only just include the area of the Serenitatus impact (Apollo 17) and after about 4.20Ga no zircon-forming magmatism occurred at this site. Magmatism continued at a reducing rate at the Apollo 14 site until about 3.90Ga, when it also ceased.

Reference

Chemical and isotopic variations of surface waters at a small catchment scale, lithological vs biological controls (the Strengbach case).

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The accurate determination of parameters controlling the chemical composition of surface waters is important for a correct modelling of the future evolution of the ecosystems in response to external forcing such as climate and human activities. Among these parameters, vegetation plays an important role in affecting movement, cycling and fractionation of elements.

In this general framework, a detailed study of the geochemical variability of the surface waters of the Strengbach catchment was carried out. The catchment is a small-forested watershed, about 80ha in surface area, in the Vosges Mountain, France (Observatoire Hydro-Géochimique de l'Environnement; http://ohge.u-strasbg.fr). It is located on a Hercynian granite, which was more or less hydrothermally altered.

During two hydrologic cycles (2004-2006), the stream at the outlet of the watershed, as well as all springs welling up located at different altitudes from various hillsides, were regularly sampled. Major and trace element (Sr, Rb, Ba, U) concentrations and Sr isotope ratios on the dissolved load of the water samples were determined.

The data highlight the large spatial variability of the chemical and isotopic composition of the surface waters of the Strengbach watershed. The variations of the mineralogical characteristics of bedrocks and soils, which are especially related to the more or less hydrothermalized character of the bedrock, can account for the spatial geochemical variations observed among the different springs of the watershed.

The data also outline an important time variation of the chemical and isotopic composition of water samples within each spring. It can be shown by using mixing diagrams, such as $^{87}$Sr/$^{86}$Sr vs. Ca/Sr, that rain contribution is not an important parameter explaining the time variation. In addition, a simple binary mixing model between two water end-members, even with variable contribution versus time, cannot account for the observed geochemical variations. The latter imply the occurrence of specific chemical fractionations unrelated to lithological parameters, but probably induced by chemical recycling through the vegetation.

The results of our spatial and time variability study of surface waters at a small watershed scale point out how such a geochemical approach can help understanding the quantification of vegetation impact on the geochemical budget.

Processes and sources during late Variscan dioritic-tonalitic magmatism (Gęśniec Intrusion, Bohemian Massif)

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Tonalitic–dioritic intrusions are common in orogenic settings. Two groups occur, emplaced at different stages of orogenic development: syn-collisional, pre-dating the main granite emplacement stage and post-collisional, contemporaneous with or post dating granite magmatism. Diorites and tonalites together with basaltic–andesitic volcanics are often the most mafic rocks present in orogenic and are often taken as end members that interacted with crust to produce a range of more felsic magmas and/or as the heat source for melting of the crust. However, diorite–tonalitic intrusions are often characterised by variable isotopic and trace element compositions suggesting that they themselves underwent differentiation and contamination.

The Gęśniec Intrusion (GI, 294-307 Ma, Bohemian Massif) represents a post collisional Variscan dioritic-tonalitic intrusion, generated during lower crust and lithospheric mantle delamination. Similar incompatible element ratios suggest a common source for the tonalite – diorite rocks in the GI, this source is distinct from that of earlier Variscan diorite-tonalite magmatism (syn-collisional, 340-350 Ma) in the Bohemian Massif. The parental magmas for the post-collisional GI were probably tholeitic, water-undersaturated basalts derived from unmetasomatised mantle that interacted with crust. Parental magmas for 340-350 Ma diorite-tonalite magmatism were basalts derived from subduction-modified mantle (e.g. Janousek et al. 2000).

In situ Sr isotope and trace element analyses of the GI plagioclase yield a range of 0.7069-0.7091, greater than that of whole rocks (0.7069-0.7084). Trace element and isotopic compositions of plagioclase suggest that different samples represent different processes of magma evolution from assimilation of wall rock by crystal mush at the magma chamber boundary, to interaction with water-rich magmas. The main differentiation recorded in plagioclase is thought to have occurred in the lower crust, below the level of emplacement of the GI and was followed by decompression and extensive resorption of plagioclase. The GI represents therefore an assembly of magmas derived from similar sources, but having undergone separate differentiation processes before final emplacement.

Reference
PAHs in sediment cores from an estuary in south of Brazil

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The temporal and spatial distribution of 14 selected PAHs, amongst the 16 priority pollutants have been analysed in the estuarine system of Guaratuba Bay, Paraná State, in the south region of Brazil. Two dated sediment cores of approximately 40 cm each were collected on the inner sector and close to the mouth to the sea of the estuary, which is approximately 15 km long. The sedimentation rate is estimated to be 6.1 mm/year and 5.2 mm/year accordingly to 210Pb and 137Cs geochronologies, respectively (Sanders et al., 2006). The surrounding region is not highly industrialised, with agriculture of banana and rice being the main economic activities, followed by fishery, aquaculture and tourism, the latter suffering a rapid increase in the past years due to the scenic landscape of the region. A moderate drainage basin encompasses the estuary, consisting of 1,724 km² and two main rivers alone, Cubatão and São João, introduce as much as 80 m³/s of freshwater into the bay. Despite of that, it is well known that PAH are ubiquitous contaminants in the environment and the use of marine sediments to reveal levels of environmental quality have been extensively reported in the literature, as they are a sink for such hydrophobic compounds. In order to quantify the distribution of PAHs along the sedimentary record, the following individual compounds were analysed in 21 sections of the cores: naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno-[1,2,3cd]pyrene. The analyses were carried out using a HPLC coupled with a fluorescence detector. The total PAH concentration ranged from 1.5 to 3,126.8 ng/g (mean 494.9) of dry weight, and the PAHs up to four rings were the most abundant. Among these, phenanthrene and fluoranthene showed the highest concentrations. Apparently, diagenetic processes, rather than petrogenic or pyrogenic inputs, play an important role in the distribution of phenanthrene along the sedimentary column, as proposed by Wakeham et al. (1980).

References

Pb isotope provenance study of Irish Bronze Age gold using LA-ICP-MS

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The Bronze Age is seen to represent a critical stage in European prehistory because of the widespread deployment of a range of distinctive materials (e.g. amber, jet, gold) in the construction of different social identities including strategies of status differentiation. Understanding the control of access to these materials and their trade and exchange is key to understanding the new social structures that arise. In Ireland, the deposition in lakes and bogs of large gold artefacts such as lunulae and torcs is one of the most striking features of the Bronze Age. But many of these artefacts are without context, having been found by turf cutters, or lack any associated archaeology. While it is clear gold is an important and special material, it is difficult to integrate the artefactual evidence with what is known of the archaeology and social structure of the Bronze Age.

Here we present the preliminary results of a lead isotope study of Irish Bronze Age gold artefacts using the novel technique of laser ablation ICP-MS. We show that the lead isotope variation in Ireland is sufficient to differentiate sources of gold, and that the required precision of lead isotope measurements can be attained for the necessarily small samples from artefacts using laser ablation. In Late Bronze Age artefacts, where the gold has been alloyed with copper, lead mixing lines can be obtained, which may allow the sourcing of both the copper and the gold.

These and future results will complement existing microchemical studies that have suggested changing access to gold resources through the Irish Bronze Age, and will provide the basis for models of gold procurement, trade and exchange.
**Experimental constraints on the origin of alkaline basalt: Evidence for a metasomatized lithospheric source**

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Due to the difficulty of explaining the high trace element and isotopic compositions of alkaline magmas from oceanic islands and alkaline massifs by simple peridotite melting, a recycled oceanic crust component is often assumed to be present in the source of these rocks. Alternatively, this component may be recycled oceanic or continental lithosphere that contains metasomatic veins. Coupled major and trace element models for the formation of alkaline lavas can provide important constraints on this debate. At present, no experimental studies have successfully reproduced the range of alkaline basalts found in ocean islands or continental massifs.

We present the results of melting experiments on natural clinopyroxene hornblendite and hornblende lithologies from the French Pyrenees conducted at 1.5 GPa and 1150-1350°C, and explore the alternative hypothesis that OIBs result from partial melting of recycled metasomatized lithosphere. The compositions of low-degree melts in experiments on both amphibole-bearing lithologies are controlled by kaersutite breakdown and are strongly ne-normative and silica-poor. K₂O/Na₂O, Al₂O₃/TiO₂ and CaO/Al₂O₃ ratios in the experimental partial melts are similar to silica-poor basanites found in oceanic islands and continental alkaline massifs. Moreover, the incompatible trace element patterns of the glasses overlap those of silica-poor lavas in both tectonic settings. A second set of experiments was done using a layer of hornblende sandwiched between layers of moderately depleted peridotite (DMM1) at 1.5 GPa and 1225-1325°C, and demonstrates that the reaction of partial melts of amphibole-rich veins with surrounding peridotite can explain the observed compositional transition between basanite and alkali basalt. The higher SiO₂ content (4-5 wt%) observed in melts from the sandwich experiments relative to those containing just an amphibole lithologies reflects the dissolution of orthopyroxene in the peridotite layers in the sandwich runs.

Our results support the hypothesis that partial melting of metasomatized lithosphere (i.e., peridotite-amphibole-bearing veins) generates alkaline basalts in continental settings [1] and that recycling and partial melting of such veined lithosphere can also contribute to the compositional characteristics of oceanic alkaline lavas. Further, the isotopic characteristics of both HIMU and EM-type OIBs are consistent with plausible models of amphibole-bearing vein formation and the resulting element fractionations [2]. Thus, recycling of metasomatized lithosphere should be considered as a viable, testable alternative to widely accepted models of OIB formation that invoke recycling of oceanic crust ± sediments.


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**AFM observations of dissolution and growth on anhydrite (100), (010) and (001) cleavage faces**

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Anhydrite is a common calcium sulphate mineral which can coexist with gypsum in evaporitic and diagenetic rocks. Textural relationships between both minerals often indicate that gypsum crystals form after previously crystallised anhydrite, through a process that involves the coupling between dissolution and crystal growth reactions. In this work, we present *in situ* Atomic Force Microscopy observations of the interaction of anhydrite (100), (010), (001) cleavage surfaces with deionised water and CaSO₄ aqueous solutions. In water, anhydrite faces dissolve at different rates and exhibit specific nanotopographic features (e.g. etch pit shapes, retreating and stabilisation of certain step directions, etc.) that can be justified on the basis of the Hartman-Perdok Theory. In contact with CaSO₄ solutions, the growth of metastable monolayers (~3.5Å in height) is promoted on both anhydrite (010) and (100) faces (the growth on anhydrite (001) faces was not observed). The monolayer develops jagged edges that form defined angles with the original steps on anhydrite surfaces. Moreover, as occurs in the case of dissolution, the growth of monolayers over anhydrite (010) and (100) surfaces is highly anisotropic, revealing a strong crystallographic control. The nature of such monolayer is discussed on the basis of both crystallographic and thermodynamic arguments.
Oriented overgrowth of brushite (CaHPO₄·2H₂O) on gypsum (CaSO₄·2H₂O)

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At slightly acidic conditions and 25º C, the interaction between aqueous solutions containing dissolved P(V) and gypsum results in surface precipitation of brushite (CaHPO₄·2H₂O) crystals. These crystals grow oriented onto gypsum’s surface, forming an epitaxy. Using an A-centered unit-cell setting for both brushite (Aa) and gypsum (A₂/a), the determined epitaxial relation is (010)₆₆ || (010)₆₆, [001]₆₆ || [001]₆₆, and [100]₆₆ || [100]₆₆. In the performed experiments, the obtained morphologies of brushite consist of thin crystals elongated in the [101] direction with {010}, {111} and {111} as major forms. In the present work, both crystal morphology and epitaxial orientation are approached on the basis of the bond arrangement within the structure of both mineral phases.

Figure 1: SEM image of thin brushite crystals oriented onto gypsum’s (010) face, along [101] direction.

Sequential Metal Extraction procedure as applied to sediments in Acid Mine Drainage environments (Aljustrel, Portugal)

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Acid Mine Drainage (AMD) is a serious environmental concern caused by mining activities and presents severe consequences to surface and underground water systems. In this work we have studied the partitioning of trace metals in sediments from AMD systems in the area surrounding the Aljustrel Mines (Iberian Pyrite Belt), using a modified Sequential Metal Extraction (SME) procedure.

Authors acknowledge that SME methods are useful to study metal partitioning in sediments. However, there are several problems with these methods, including the one of Tessier et al. (1979). Among these are: trace element redistribution among phases, nonselectivity of extractants, and sulphide dissolution during organic matter oxidation steps. In order to overcome these difficulties the proposed method combines modifications from Hirner (1996) and Breward et al. (1996). The oxidation of organic matter is performed separately by first extracting it from the sediment. The six-step sequential extraction procedure was performed on streambed sediments of Ribeira de Água Forte (Aljustrel). The extractant solutions were analysed by AAS for selected trace metals (Cu, Zn, Pb, Ni, Cd, and Co).

Cu, Pb, and Zn have the highest averaged relative concentrations in the sediments (51%, 27%, and 14%, respectively). Ni, Cd and Co exhibit low values (< 4%). In contrast to these results in the sediments, water analyses show higher Zn concentrations in relation to Cu, suggesting a preferential sediment-water partitioning for Cu. Also shown is the anomalous character of an iron-rich sample in relation to the correspondent water, where a peak in all elements is observed. This sample is also exceedingly anomalous in Cu for reasons currently unknown to us. In relation to the different phases, organic matter has no important role in the adsorption processes (1.7%). Trace metals occur preferentially bound to iron oxide phases (70%), followed by non-specific adsorption (25%).

References

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Chemical compositions of zircon from an U-mine area, Portugal

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The Vale de Abrutiga U-mine consists of quartz veins containing wolframite, sulphides and secondary saléeite and metasaléeite.

One hundred thirty seven chemical analyses of zircon were obtained by electron-microprobe from unaltered and altered biotite granite, mineralized quartz veins, phyllite and quartzite of regional metamorphism and phyllite adjacent to mineralized quartz veins from the Vale de Abrutiga U-mine area, central Portugal. Chemical composition of zircon is highly variable. Zircon from altered granite is the richest in P, Y and Fe\textsuperscript{3+} and contains on average 0.22 wt. % UO\textsubscript{2}, but values up to 0.50 wt. % UO\textsubscript{2} were found in the analyses with low totals (~84.69 wt. %). Distribution of U in some of these individual altered grains shows a chemical zonation expressed in the rim containing more U than the core. The core has a chemical composition similar to that of zircon from unaltered granite. Zircon from quartzite has the highest content in Zr and the lowest of Fe\textsuperscript{3+}. Zircon from phyllite adjacent to quartz veins has higher U content than zircon from phyllite of regional metamorphism, which does not contain U. Zircon from mineralized quartz veins is dissolved and vacuolated. The grains have cores chemically close to the endmember [(Hf,Zr)SiO\textsubscript{4}], but rims are hydrated, have very low totals (~82 wt.%), low SiO\textsubscript{2} (~14 wt.%), and ZrO\textsubscript{2} (~40 wt.%). contents and very high Fe\textsubscript{2}O\textsubscript{3} (~8 wt.%), and UO\textsubscript{2} (~18 wt.%). contents. The anomalous zircon rims were lately formed from U-rich supergenic solutions. Enrichment in U is a characteristic of altered zircon from the mineralized quartz veins and from altered Variscan granite. The high U contents found in rims of the altered zircon from altered granite and mineralized quartz veins are associated to high Fe contents. It is well known that uranium sorption on Fe oxyhydroxides is an important process. Therefore the very high U-enrichment found in rims of altered zircon grains can be due to the presence of these Fe oxyhydroxides.

The Vale de Abrutiga U-mine was formed in lithological and structural traps by U-rich solutions derived from meteoric water, warmed by deep circulation, and enriched in U by the solubilisation of U-minerals from granites (uraninite, monazite). Uranium from U-rich solutions percolating through the quartz veins was later adsorbed by the most altered zircon or by Fe oxyhydroxides which formed in the most altered rims of zircon crystals.

3-D modeling of iron ore deposit in Chadormalu area in the Central Iran

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Chadormalu iron ore deposit is one of the biggest iron ore in Iran. That is located in the Central Iran and excavates iron ore in this area. Chamomile reverse fault and Kankani right lateral strike slip fault shear and deform ore deposit. Asymmetric ore deposit shape and faulting are some reasons that excavators have problems for exploration. Expansion of iron ore, distribution of contaminated ore (for example apatite) and recognized of blind faults concludes with use chemical analysis and logging boreholes data in deferent topographic levels. Deferent topographic levels data merge and design under ground 3-D models iron ore. Iron ore deposit is flattening and its strike is northwest - southeast. Iron ore massive dip is high angle and its dip direction is southwest. Stratigraphic iron ore boundaries are faulted and high angle. A lot of many strike slip fault distinguish with north - south strike into ore body. Designed 3-D models can be show best location for start of excavation. Therefore, we can subdivide ore deposit to several quality parts.
Radiogenic $^{26}$Al chronometry of evaporites

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Radiogenic production of $^{26}$Al in Na rich evaporites can potentially be used for chronometry over several million years. This can be a tool for dating paleoclimate conditions in arid environments. Measurable quantities of $^{26}$Al are present in material with either high concentrations of alpha emitters (principally U and Th) or high concentrations of target nuclei. Significant quantities of $^{26}$Al are recorded in U and Th ores, and the primary mechanism of this production is the $^{23}$Na (α, n)$^{26}$Al reaction (Sharma and Middleton, 1989). Measurable quantities of $^{26}$Al should, therefore, also be present in material with modest concentrations of U and Th, but high concentrations of Na. To test this potential geochronometer, a review of the available cross-sectional data for this reaction, as well as the U, Th, and Na composition of various evaporites was done. We will present preliminary data testing the feasibility of this method.

The $^{238}$U and $^{232}$Th decay chains are the dominant natural alpha sources, with a total of 8 alpha particles emitted in the $^{238}$U decay chain and 6 from $^{232}$Th decay. The range of alpha particles in rocks is generally less than a few tens of microns, and the alpha-emitters contained within the evaporite minerals themselves are the principal mechanism of radiogenic $^{26}$Al production. Since U is soluble in water, and Th is largely insoluble, many evaporite deposits have high U/Th. Disequilibrium in the U-series decay chain occurs in subaqueous deposits over the time range of this potential chronometer, and excess of $^{234}$U over $^{238}$U in evaporites will result in higher $^{26}$Al production.

Saline minerals, which are common in marine, lacustrine, hydrothermal, and soil deposits are high in Na and low in Al. Calculated $^{26}$Al production rates for U in secular equilibrium is ~10 atoms/gramNa/ppmU, and minerals such as halite, glauberite, and trona are 30 to 40 weight percent Na. The range of measured and previously reported U concentration in salts varies from a few ppt to several ppm. Exceptionally pure salts incorporates less U, but also contain less stable Al. Al concentrations in salts range from 1.5-150 ppm. At these concentrations, production rates are comparable to cosmogenic $^{26}$Al at the surface. A salt with 10 ppm Al and 1 ppt U should contain detectable $^{26}$Al in less than a century.

Reference

Oscillatory zoning fahlores from Au-Ag epithermal deposits

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Results

Oscillatory zoning was found in tellurian fahlores (goldfieldites) \([(Cu,Ag)_{10}(Fe,Zn)_{2}(Te,Sb,As)_{3}(S,Se)_{13}\)] from three epithermal Au-Ag deposits: Prasolovskoe, Ozernovskoe (Kamchatka-Kuril arc, Russia), and Elshitsa (Sredna Gora zone, Bulgaria). Two types of oscillatory zoning were revealed.

(1) Multiphase (or heterophase) with successive deposition of different minerals or mineral assemblages e.g. Elshitsa where there is regular alternation of goldfieldite bands (Te 2 to 3.2 apfu) with bands (1-2 to 50-100 µm) of tellurian-tennantite (Te 1.5 to 2 apfu) with abundant inclusions of native tellurium. At Prasolovskoe there are “chains” of hessite grains that occur within goldfieldite with a period of 10-20 µm.

(2) Monophase oscillatory zoning reflects element fluctuations in the chemical composition of a mineral. At Elshitsa it is represented by variations of Te from 2.3 to 3.2 apfu and As from 1.8 to 0.7 apfu with a period of 2-3 to 10 µm. At the Ozernovskoe deposit Te ranges from 1.25 to 2.5 apfu, and Sb from 0.86 to 1.33 with a period of up to 20 µm while As increases from 0.75 to 1.63 apfu.

Discussion

The number of such zones in grains with multiphase zoning is usually the same for all crystals in the sample which means that multiphase zoning was caused by an external factor, e.g. due to fluctuation of H₂S and O₂ activities in the solution, and can be described by the equation:

\[
(Cu,Ag)_{10}(Fe,Zn)_{2}(Te,Sb,As)_{3}(S,Se)_{13} + 2.8Te + 2.6H₂S + 0.4H₂O + 2.8O₂ = 1.2(Cu₁₀Te₄S₁₃ + 2As(OH)³)\]

Monophase zoning is caused by an internal factor, e.g. by the difference between velocities of absorption of any component and its diffusion in the growing zone of the crystal. Since such a zoning occurs only in non-stirred solutions and can indicate local stagnation of the fluid.

Conclusions

Oscillatory zoning can be caused by both external and internal mechanisms and contain important information on mineral forming conditions.

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References

Terrestrial atmospheric nitrogen in lunar soils?

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Surface-correlated N in lunar soils and breccias exhibits an obvious but mysterious effect that was evident essentially from the first analyses of samples returned by the Apollo missions: The isotopic ratio $^{15}$N/$^{14}$N is variable, by up to 30%. For some time this was interpreted in terms of variation in the solar wind isotopic composition, perhaps reflecting solar nuclear processes and perhaps even reflecting a secular trend (e.g. Kerridge, 1993). This would be very difficult to understand (Geiss and Bochsler, 1982) in terms of the standard model of the Sun, however, and more recently Hashizume et al. (2000), among others, have championed an alternative interpretation that the isotopic variations reflect N in extralunar, extrasolar particle infall mixing with the solar wind N.

Most recently, Ozima et al. (2005) have suggested another interpretation: That the isotopic variations in lunar soil N reflect admixture of solar wind N with an "Earth wind" flux of atmospheric N. An Earth wind flux is quantitatively insufficient under present circumstances, but might have been quantitatively effective very early in the history of the Earth-Moon system, before the development of the global geomagnetic field. Although viable this seems a quite unlikely hypothesis, but one laden with important consequences if valid.

The Ozima et al. (2005) hypothesis is also subject to simple test: If the isotopic variations are due to a contribution of Earth wind they should be essentially absent in lunar farside samples, since the Moon is thought to have been spin-locked essentially throughout the history of the Earth-Moon system, and an Earth wind would not reach the farside. The purpose of this work is to apply this test.

There are no samples returned from documented farside locations, but there are numerous lunar meteorites, half of them presumed to originate on the farside. We analyzed N in nearly all eleven soil and fragmental breccias known among Antarctic lunar meteorites. By the Earth-wind hypothesis, half should display essentially constant isotopic composition of N, at the solar wind value. This expectation is not realized in our observations, so we conclude that the Earth-wind hypothesis for the origin of N isotopic complexity in lunar soils is not tenable.

References


The rim structure of simple craters as an indicator for an impact vector

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The rims of two simple impact craters, Wolfe Creek, Australia, and Meteor Crater, AZ, USA, were examined. New methods of analysis were devised to display structural features that may be indicative of oblique impacts. Data from the two craters are compared.

Although the majority of craters are formed by oblique impacts, crater shapes remain circular for impact angles >30° and thus normally do not give any implications for the direction of impact. However, the ejecta blanket is the most sensitive indicator for impact angle and direction, and can show a “forbidden zone” on other terrestrial bodies.

The ejecta trajectories forming asymmetric or bilaterally symmetric ejecta blankets of oblique impacts may deviate from a radial orientation with respect to the final crater center and could probably be traced at the rim and overturned flap of simple craters, which represent the most proximal part of the ejecta. We therefore systematically analyzed strike and dip of strata in the crater rims of two young, simple impact craters, Wolfe Creek Crater and Meteor Crater.

Wolfe Creek Crater is located in Western Australia, was formed 300 ka ago and has an average diameter of 880 m. It was formed in sub-horizontal Devonian sandstones that are overlain by a layer of Miocene laterites. Meteor Crater in Arizona is 50 ka old and 1200 m in diameter. Pre-impact target rocks are sub-horizontal Permo-Triassic sandstones and limestones.

The strike data collected in both craters is translated from a geographic to an azimuthal reference scheme with the point of origin situated in the crater center. The strike of rock layers in the rim is examined for deviations from a hypothetical concentric orientation with regards to the crater center. The deviation can be expressed as an angular value for each measurement.

Results: When displayed in a polar plot, which gives a better sense of the spatial relationship, the values reveal a bilaterally symmetric orientation of the bedding and potential “forbidden zones”. These preliminary results contradict earlier propositions for an impact vector in both Wolfe Creek Crater (Shoemaker et al., 2005) and Meteor Crater (Roddy & Shoemaker 1995). We intend to compare these results with other information, e.g. distribution of dip data, stereo plots and spatial relationships of bedding in three dimensions.

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References

The influence of weathering processes on riverine Mg and Li isotopes in rivers draining basaltic terrain

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Chemical weathering of continental Ca-Mg silicates is a long-term sink of atmospheric CO₂, and therefore exerts a major control on climate. However, tracing change in weathering processes through time is difficult because many traditional radiogenic isotope tracers yield ambiguous signals. The transfer of Mg from the continents to the oceans, and its subsequent removal from the oceans, plays a major role in the global carbon cycle, and has also been invoked as a dominant control on oceanic carbonate chemistry. However, the relative importance of these processes, as well as those which fractionate Mg isotopes during weathering, are not well understood. Distinguishing Mg isotope variations which arise from differences in lithology from those caused by weathering processes is difficult, because the range of δ²⁶Mg observed in different rock types is large. However, the study of monolithological terrains offers one way of circumventing the effects from different rock types.

This study presents Li and Mg isotope data for bedload, suspended and dissolved load of rivers from basaltic catchments in Iceland. In addition, primary basaltic mineral phases and soils have also been analysed to determine the possible effects of weathering of primary minerals and the formation of secondary phases.

Li isotope (δ⁷Li), variations are generally thought to reflect the balance between dissolution of primary minerals and secondary mineral formation; the light isotope, 6Li, is preferentially taken up by secondary minerals. The δ⁷Li of the dissolved phase varies between +17 and +44‰, and generally decreases downstream.

δ²⁶Mg values of the river sediments range from -0.83 to +0.83‰ relative to DSM-3. Basaltic soils have variable δ²⁶Mg; those with a higher secondary mineral content are isotopically lighter. Co-variations of riverine δ²⁶Mg with suspended load δ²⁶Mg, as well as with pH and the fraction of Mg lost to clays appear to indicate that the isotope composition of the dissolved load is dominantly controlled by preferential uptake of ²⁴Mg into clays, leaving the residual dissolved load isotopically heavy.

These data suggest that Mg isotopes in basaltic rivers are dominantly controlled by secondary mineral formation, and thus the degree of chemical weathering.

Carbon isotope evidence (¹³C and ¹⁴C) for fossil methane-derived dissolved organic carbon from gas hydrate bearing cold seeps

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Vast reservoirs of gas hydrate in continental margin sediments have the potential to influence the properties of organic matter in both sediments and the overlying water column. Natural radiocarbon and stable carbon isotopes were utilized to determine if fossil methane-derived carbon associated with gas hydrate-bearing sediments was incorporated into the dissolved organic carbon (DOC) of both sediment pore waters and overlying near-bottom waters from northern Cascadia margin cold seeps. Pore water DOC from the sulfate-methane transition (SMT) had a δ¹³C of -60‰ at a site with a microbial methane source and -45‰ at a site with a thermogenic methane source. In both cases, methane-derived carbon was the predominant carbon source (80-100%) for DOC associated with the SMT. Furthermore, ¹⁴C- and ¹³C-depleted bottom water DOC from the thermogenic gas hydrate site indicates that methane carbon constituted 30-50% of the bottom water DOC. Our results indicate that fossil-derived sources of carbon were a significant component of DOC in the cold seep systems we investigated, and suggest that fossil methane-derived DOC fluxes from cold seep sediments may contribute to the aged DOC pools of the deep open ocean.
Neon and plume – MORB mixing along the Galapagos Spreading Center

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Characterizing noble gas composition variations along plume-influenced ridges can help reveal mantle processes such as mantle flow, source mixing, degassing, fractionation and mantle heterogeneities. Lavas from Western and Southern Galapagos islands have very high 3He/4He, up to 30 Ra, but the Northern Galapagos islands and Wolf-Darwin lineament have relatively low 3He/4He, between ~6 and 8 Ra. Along the Galapagos Spreading Center (GSC), 3He/4He ratios are from 5.9 to 8.5. No high 3He/4He ratios resembling those of Western and Southern islands are observed along the GSC, despite many indicators of the involvement of plume-derived material [1]. Here, we use Ne isotopes to detect plume involvement in the generation of GSC basalts.

New basaltic glasses were sampled in the ridge axis of GSC between 86 and 98°W. The samples were analysed by crushing of one fragment of sample in order to release volatiles trapped in vesicules. The abundance of CO2 was measured with a capacitance manometer and the isotopes of Ne were analysed on a Helix MC noble gas multi-collection mass spectrometer.

Preliminary results from two samples so far analysed have very low abundances of mantle Ne, with 4He/21Ne* (where * denotes corrected for atmospheric contamination) significantly higher than the mantle production ratio. Fractionation of He from Ne may result from late stage degassing (during emplacement of the lavas, for example) or could be due to contamination of the plume-derived melts by asthenospheric He (but no Ne). Analysis of more samples, as well as analysis of Ar isotopes and abundances, will allow two cases to be distinguished.

References
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Significance of the mantle Fe isotope variations

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The Fe isotopic variability found among mantle xenoliths [1] is in sharp contrast with the homogeneous isotopic composition of mantle-derived rocks [2,3]. To address this issue, we have undertaken a comprehensive petrological and geochemical study of different suites of mantle xenoliths. They sample continental and oceanic lithospheric mantles of different ages, in the spinel facies and the garnet facies.

The δ57FeIRMM14 range measured at the bulk rock scale (99‰) is even larger than previously found. None of the xenolith suites studied display a homogeneous isotopic composition. Bulk-rock Fe isotope signatures were compared to bulk-rock and mineral major and trace element contents. In some cases, the observed correlations can be interpreted as resulting from the effect of different types of metasomatism whereas for other examples, they seem to reflect melt extraction. Although both of these processes affected the bulk-rock Mg#, it was possible for three of the studied xenolith suites to infer the “starting” isotopic composition of the mantle area studied. Two intracontinental suites (Cameroon and South Africa) yielded a δ57FeIRMM14 of 0.1‰, whereas one intraoceanic suite (Kerguelen) led to a value of 0‰ for a highly melt-depleted mantle.

These results point to an “initial” lithospheric mantle, prior to multiple episodes of metasomatism and melt extraction, having a mean δ57FeIRMM14 indistinguishable from that of mantle-derived basalt. This inference is consistent with [4].

These findings also illustrate that Fe isotopes are a sensitive tracer of mantle metasomatic processes despite the high temperatures involved and the usually small Fe isotopic variations observed in igneous rocks. The mechanisms responsible for this peculiar behaviour of Fe isotopes has yet to be fully understood.

References
Plagiogranitic ocelli in the pillow lavas of the Eoarchean (3.7-3.8 Ga)
Isua greenstone belt, SW Greenland

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Pillow basalts in the 3.8-3.7 Ga Isua greenstone belt, West Greenland, contain randomly-distributed white ocelli structures. The ocelli are composed predominantly of polycrystalline Na-plagioclase and quartz, with minor hornblende and biotite. They are devoid of any radial and concentric internal structures and display all stages of coalescence. Compositionally, the ocelli are calc-alkaline dacites, whereas the surrounding matrix is a tholeiitic ferrobasalt, suggesting that ocelli melts were not derived from the melts of basaltic matrix by fractional crystallization. Similarly, transition metal and REE abundances cannot be explained by simple closed-system crystal fractionation of mafic liquids. High concentrations of Ni (120-270 ppm in ocelli; 105-160 ppm in matrix), Cr (395-570 ppm in ocelli, 330-590 ppm in matrix), and Co (25-45 ppm in ocelli, 54-64 ppm in matrix) are consistent with near-primary mantle-derived dacites, whereas the surrounding matrix is a tholeiitic ferrobasalt, suggesting that ocelli melts were not derived from the melts of basaltic matrix by fractional crystallization. Similarly, transition metal and REE abundances cannot be explained by simple closed-system crystal fractionation of mafic liquids. High concentrations of Ni (120-270 ppm in ocelli; 105-160 ppm in matrix), Cr (395-570 ppm in ocelli, 330-590 ppm in matrix), and Co (25-45 ppm in ocelli, 54-64 ppm in matrix) are consistent with near-primary mantle-derived melt compositions. On the basis of chondrite-normalized REE patterns, the ocelli are divided into two groups. Group 1 is characterized by LREE-depleted patterns, whereas Group 2 displays LREE enrichment. The trace element characteristics of the Group 1 ocelli are similar to those of the surrounding matrix. Both the ocelli and matrix are depleted in Nb relative to Th. Geochemically the Isua ocelli and host volcanic rocks closely resemble those of Phanerozoic supra-subduction zone ophiolites. Given the pronounced depletion of Nb, relative to Th and LREE in the Group 2 ocelli and picritic to basaltic host rocks, partial melting of a forearc mantle wedge, fluxed with subduction-derived LREE-rich hydrous fluids or melts, is favoured for the source of the Isua ocelli and host volcanic rocks. The ocelli-bearing island arc picrites are structurally juxtaposed against a boninitic volcanic association [1]. Recently, the presence of a relict sheeted dyke complex has been reported within the picritic to basaltic island arc volcanic association, indicating that the Isua greenstone belt was formed by sea-floor spreading in a supra-subduction zone setting [2]. The presence of plagiogranitic ocelli is also consistent with an ophiolitic origin of the Isua greenstone belt.

References

Cathodoluminescence behaviour of Mn-rich carbonates

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It is well known that manganese is the most important cathodoluminescence activator in carbonates (Pagel et al., 2000). However, the CL method is rarely applied in the petrological investigation of Mn-carbonate-bearing rocks and mineralizations due to the commonly accepted effect of concentration quenching or self-quenching, which occurs at elevated Mn concentrations. A comprehensive knowledge about the luminescence behaviour of Mn-rich carbonates still does not exist. The purpose of our study was to determine the effect of Mn concentration on self-quenching.

The cathodoluminescence behaviour of Mn-rich carbonates (rhodochrosite, Ca-kutnohorite, Mn-rich calcite) from hydrothermal and volcano-sedimentary systems was preliminarily studied by CL microscopy and spectroscopy. Chemical composition of carbonates was investigated by X-ray diffraction and FTIR spectroscopy methods. Most of the samples showed bright orange-red CL. The brightest CL occurred in the 5 to 14 wt% range of Mn content. A strong decrease of CL intensity was observed between cca. 14 and 18 wt% Mn, but the rhodochrosite samples with 37 to 45 wt% Mn are still dull luminescent. The study by CL spectroscopy indicated a 620 nm maximum peak position for calcite, 640 nm for rhodochrosite and 630 nm for a Ca-kutnohorite with 9 wt% Mn (Fig. 1).

Figure 1. CL spectra of rhodochrosite, Mn-rich calcite and Ca-kutnohorite with 9 wt% Mn

Our results show the existence of cathodoluminescence in carbonates characterized by elevated Mn concentration (5 to 45 wt% Mn). It seems that self-quenching is not complete even in the case of rhodochrosite.

References
**Did hydrothermal fluids contribute to the huge Úrkút Manganese ore body?**

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Deposition of the black shale-hosted Úrkút Mn carbonate deposit in Hungary occurred in the Early Jurassic. The ore body formed in a structurally controlled marine basin via bacterially mediated, early diagenetic formation of Mn carbonates. It has been proposed that hydrothermal fluids venting into the depositional basin was involved in the mineralization, but this idea is controversial. A hydrothermal origin may be supported by several lines of evidence such as the fractionation of Mn and Fe, the in situ precipitation of celadonite and other clay minerals, and the accumulation of huge amounts of Mn, Fe, Si. However, none of these evidence alone or together for that matter are conclusive and the aim of this study is to look for evidence for a hydrothermal plumbing system by study of the underlying Mn- and Fe-oxide mineralization. Analysis of 12 samples show a wide range of Mn and Fe contents, with mean values of 35.9% Mn and 10.3% Fe, Si (4.9%), Sr (mean 0.6%), P (0.3%), Ba (0.3%) and Co (0.07%) are enriched in the Fe-Mn oxides. The Fe/Mn mineralogy of the samples is cryptomelane, todorokite, manganite, goethite, hematite, groutite. Polished thin sections show signs of bacterial activity and the precipitation of Mn oxides within soft carbonate sediments, sediment that was later partly to completely replaced by a later stage of Mn oxides. Sr and P enrichments reflect input from leaching of carbonates and organic matter. Mn oxide and Mn carbonate mineralization occur above a thick carbonate basement cut by deep fracture zones. Our data suggests that the Fe and Mn oxides were deposited from deep-sourced fluids circulating through basement rocks. Circulation along zones of structural weakness was likely driven by high geothermal gradients. Sr isotopes are being measured on these samples to confirm this idea.

**Textural and microstructural analysis of rapidly grown omphacite from eclogite facies pseudotachylytes**

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Rapidly grown omphacite (Jd40) has been formed in melt domains of an eclogitized gabbro from central Zambia by frictional melting during pseudotachylyte formation [1]. Omphacite occurs as an extremely fine-grained matrix (grain size of 2-3 µm) and form partly spherulites with diameters ranging from 100 to 300 µm. The textures point to fast mineral growth with local differences in nucleation and growth rate due to heterogeneous cooling. Here, omphacites within melt domains have been studied using electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM) to relate mineral growth texture with deformation (dislocation) microstructure under eclogite facies conditions.

EBSD analyses of a single spherulite show a common b plane for all omphacite grains within the spherulite, while there is no lattice preferred orientation for matrix omphacite. The grains within the spherulite are significantly larger than in the matrix and form radially oriented needles. TEM revealed a strong deformation microstructure with subgrain boundaries, dislocation networks and nodes as well as stacking faults and associated partial dislocations. Grain boundaries of adjacent omphacites are often interlocked and wave-like curved. The spherulitic texture is obviously formed during growth. The distinct dislocation microstructure may have originated from the differential stress developing during rapid growth. Growth related deformation microstructures are barely studied yet and will be discussed in connection with eclogite facies pseudotachylyte formation.

**References**

Evaluating magnetic susceptibility as a rapid scoping tool for assessing trace metal contaminated soils

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The widespread association in many soils of various trace metals with nano- or micro-particle grains of magnetic Fe-O-H phases has led to the proposal (Bityukova et al., 1999) that the magnetic susceptibility, \( \chi \), of soils might be used as a proxy for trace metal concentrations, particularly concentrations of bioavailable trace metals, in contaminated soils. The utility of such measurements in areas of trace metal contamination has been tested here using field and laboratory magnetic susceptibility measurements and a variety of chemical and mineralogical analyses: ICP-AES, XAS, sequential extraction, EPMA, XRD and XRF. Three contaminated sites, two in Greece (Kozani – a disused power station, Thessaloniki – the site of a tannery) and one in the UK (Potters Hill, Bolton – site of a former chromate works) were selected for study.

Good correlation of Zn and Cu with field-based \( \chi \) data was found, however a very poor correlation was found between Fe and Cr and field-based \( \chi \) data. This suggests that whilst Zn and Cu are predominately associated with phases contributing to \( \chi \), Fe and Cr occur in substantial proportions in phases with contrasting magnetic susceptibilities. EPMA mapping confirmed the existence of all of Fe-rich, Cr-rich and Fe+Cr-phases. XANES and EXAFS data were consistent with the occurrence in the soils of the Cr(III) phases with the following stoichiometries: \( \text{CrO}_3 \), \( \text{Cr(OH)}_3 \) and \( \text{FeCr}_2\text{O}_4 \). Whilst field-based \( \chi \) measurements are both cheaper and faster than chemical analysis of bulk soil or soil extracts and thereby have the potential to be a useful scoping tool, the relationship between \( \chi \) and metal concentrations may be critically dependent on the solid phase speciation of the trace metals of interest, necessitating careful consideration of data on a site-by-site basis.

Novel corresponding - states principle approach for calculating the isotopic properties of water under elevated temperatures and pressures

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The isotopic properties of geologic fluids under geologic conditions are of geochemical interest. For this reason, we developed a corresponding-state principal (CSP) formulation for expressing the equation of state (EOS) of isotopologues of molecular fluids in terms of the dimensionless three-parameter equation (Polyakov et al., 2007):

\[
Z(\tau, \delta, \omega) = Z_0(\tau, \delta, \omega) + \frac{\partial Z_0(\tau, \delta, \omega)}{\partial \omega} \omega_0 (\omega - \omega_0)
\]

where \( Z \) is the compressibility factor; \( \tau \) and \( \delta \) are dimensionless temperature and pressure, respectively; \( \omega \) is the Pitzer acentric factor; subscript “0” refers to the major isotopologue. Using this CSP formulation for minor isotopologues, we further developed a general EOS-based approach for calculating the reduced isotope partition function ratio (RIPFR) for “real-gas” fluids under elevated temperatures and pressures presented by Polyakov et al. (2006).

This novel approach was applied to the isotopologues of water (HDO and H\(_2\)O\(_{18}\)), using experimental data (e.g. liquid-vapor fractionation and molar volume isotope effects). The RIPFR of water calculated from our approach show contrasting behaviors for HDO and H\(_2\)O\(_{18}\). The D/H exhibits an overall decrease of 5‰ with increasing pressure to 1 kb, which is in agreement with experimental results for brucite-water system (Horita et al., 2002). In contrast, the RIPFR for H\(_2\)O\(_{18}\) increases by 1‰ with pressure to 1 kb. The significant pressure effects on the isotopic properties of water obtained from this study have important geochemical implications.

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References

Modelling of contact metamorphism and metasomatism near the Talnakh intrusion: Effect of fluid convection versus conductive heat transfer

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As was shown for a number of geological and theoretical models, convective heat-and-mass transfer near magmatic bodies is of great importance. The country rocks of intrusions in the Noril'sk ore district at the northwestern margin of the Siberian Craton are one such case. In this communication, mathematical modeling is used to describe the heat redistribution and fluid convection in the volcanosedimentary sequence at the contact with the Talnakh ore-bearing intrusion. The objective of this study was to simulate the temperature and hydrodynamic patterns that would fit the arrangement of isotherms and isograds, as well as the distribution of metasomatic rocks near the intrusion.

The problem of modeling of heat transfer and convective flows of a two-phase fluid is solved in the 2D setting in the Cartesian coordinate system on the basis of time-dependent equations of nonisothermal hydrodynamics with account of vapor-liquid phase transition (USGS HYDROTHERM code).

Patterns of fluid flow in the hydrothermal system with a permeable vertical zone that crosscuts the intrusion were obtained from the modeling results. The suggested mechanism of mixing of magmatic fluid with formation water may be efficient only at sufficiently high permeability of the rocks (fig. 1).

As the modeling results show, metasomatic zoning may arise at the postmagmatic stage within a zone 150-200 m thick above the intrusion and no more than 30-40 m thick below the lower contact.

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Temporal distribution and cyclicity in formation of porphyry Cu-Mo deposits

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The recent increased applicability of global paleo-reconstructions, coupled with improved geochronology from most of the world’s investigated Cu–Mo porphyry deposits, allows for an improved understanding of the distribution pattern of orogenic copper and molybdenum in space and time, as well as the relation between the resources of deposits and time of their formation. Geochronological data compiled for about 350 known large to medium (with resources > 0.05 mln. t) porphyry Cu–Mo deposits from all over the world including Asian part of Russia (Sora, Zhireken, Schakhtama, Aksug and others) and Mongolia (Kharmagtai, Tsagan-Suburga, Erdenetuin-Obo) are represented on the diagram in the time of deposit formation vs resources coordinates (Fig. 1). Data distribution and their mathematical treatment show that:

1) there is an irregularity in geochronological density of Cu-Mo resources; 2) discreteness in phases of maximum ore-forming activity (28-39; 50-60; 66-73; 75-82; 235-245 Ma) with duration up to 10 Ma; 3) in time, not every significant plume correlates with the epochs of intense ore formation; 4) spectral and wavelet-analysis of geochronological data reveals quasi-periodic cycles of 120-100, 69-60, 36-28, 20-15, 12-10, 8-7 Ma alternating at different time intervals. The latter two factors indicate the formation of porphyry Cu-Mo deposits is related not only with plumes but also with tectonic plate reorganization.

The investigations were supported by the Russian Foundation for Basic Research, grant 06-05-64860; Integration project of the Presidium of Siberian Branch and Far East Branch of RAS No. 6.1, and Grant of the Ministry for Russian Science and Education DSP.2.1.1.702.
Raman-Spectroscopy – A powerful tool for life- and material-sciences

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Raman spectroscopy has emerged in the last years as an extremely powerful method in almost all natural science disciplines. This renaissance of Raman spectroscopy was mainly triggered by the latest achievements in laser technology, by the design of very efficient filter to suppress the elastically scattered Rayleigh light, and by the development of extremely sensitive detectors. The advantages of Raman spectroscopy are its unprecedented high specificity and its versatility. Raman spectroscopy is a non destructive technique and does in general, require only minimal or no sample preparation. Solid, liquid, and gaseous samples can be measured as well as transparent or non transparent samples or samples with different surface textures i.e. Raman spectroscopy can be applied to any optical accessible sample, where a pre-treatment of the sample is not necessary.

In this presentation a report on a Raman spectroscopic characterization of a broad variety of biological probes will be given. Raman spectroscopy is an extremely capable, suitable and prominent method for probing the relationship between structure, dynamics and function of biomolecules. In this context micro-Raman imaging, the surface enhanced Raman scattering (SERS) technique and resonance Raman spectroscopy are commonly applied. These Raman techniques allow one to characterize the structure of e.g. isolated pharmacological relevant substances and the investigation of biological tissues i.e. monitoring of low concentrated active components in plants and especially the localization of pharmaceutical relevant substances in tissues. Not only the localisation but also the investigation of the mode of action of drugs against infectious diseases on a molecular level will be presented. In addition Raman spectroscopy also allows the identification of microorganisms on a single cell level.

The main focus within the second major topic material photonics is concerned with the derivation of structure-property as well as structure dynamics relationships by means of Raman spectroscopy. In particular the characterization of mineralogical samples like e.g. extraterrestrial material (meteorites) and the derivation of structure-activity and dynamic relationships in artificial light harvesting systems or photocatalysts based on Ruthenium-polypyridyl complexes by means of resonance Raman spectroscopy will be presented.

In summary the presented examples convincingly demonstrate the great capabilities of Raman spectroscopy for life and material sciences making this technique to one of the most essential laser spectroscopical methods.

Experimental evidence for rapid re-equilibration of water between melt inclusions in olivine and host magma

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Here we report the results of pilot experimental study aimed at evaluating the ability of olivine to protect melt inclusions at changable external conditions, which may readily take place in long-living magmatic systems.

For the experimental study, natural olivines containing glassy inclusions were picked from olivine-plagioclase-pyroxene phyric submarine tholeiitic basalts from the Galapagos Plateau (sample PLO2-24-33 provided by D.Christie). Ninety six inclusions from this sample were preliminarly studied for major and trace elements. Water content in natural inclusions measured by ion probe ranged from 0.37 to 0.67 wt % (n=20) and was similar to matrix glass (0.43 wt %). Selected olivine grains (0.5-1 mm) with inclusions inside were loaded in Fe-presturated Au80Pd20 capsule together with reduced (QFM-1) powder of depleted synthetic MORB. The mixture was dopped with ~ 3 wt % of distilled water. Experiments were conducted in internally heated pressure vessel at 200 MPa and 1140 °C using Ar as pressure medium. The run duration was 48 hours.

Experimental products were studied optically, with electron and ion probe. Surprisingly, all of seven inclusions analysed after experimental treatment had high water content (2.0-2.7 wt%), close to the matrix glass (2.3 wt%) and ~5 times higher than in starting compositions and exhibited high MgO (8.1-8.9 wt% vs. 4.0-6.7 wt % prior experiment) corresponding olivine-melt inclusion equilibria at hydrous conditions. Incompatible trace elements, S, F and Cl content in the melt inclusions decreased only slightly after the experiment (due to host olivine dissolution), remaining within the range of natural Galapagos inclusions and ~10 times higher than in depleted synthetic matrix.

We conclude from this study that melt inclusions in olivine behave as semi-closed system at changing external conditions. Complete re-equilibration of water between inclusions in large olivines (up to 1mm in size) and matrix melt is achieved during 2 days or less, whereas incompatible trace elements and other volatile components (S, Cl, F and likely CO2) behave as immobile. Rapid water (hydrogen) exchange between inclusions in olivine and host magma, which is faster than Fe-Mg diffusion in olivine, implies that those inclusions experienced detectable Fe-Mg re-equilibration with olivine can unlikely preserve initial water concentrations and most likely reflect water content in surrounding magma prior eruption.
Weathering of Bronze Age potsherds in a Mediterranean climate (Cres Island, Croatia)

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The aim of this study was to study the causes of well preserved status of potsherds in bronze age hill forts on Cres island (Northern Adriatic Sea) exposed to Mediterranean climate and their buried equivalents in colluvial deposits. The island of Cres has a long history of settlement and hosts some very important Mesolithic, Neolithic and Bronze age sites. Due to erosion large areas are bare karst lacking soil cover and prehistoric potsherds can be found in stonewalls of hill forts or caves.

The potsherds were analyzed by microscopy methods as well as geochemistry to study the weathering process in both exposed and buried potsherds. The colluvial soil containing potsherds was dated at Beta Analytic AMS facility (Beta-199264) and a calibrated ¹⁴C date ranging from 2030 to 1870 BC was obtained. Under the optical microscope, the potsherds are texturally homogeneous and display inclusions of similar type, abundance, and grain size.

The enrichment of Ca in exposed potsherd rims is accompanied by depletion of light REE’s and enrichment of heavy REE’s.

The results show that potsherds exposed to the Mediterranean climate for four thousand years have an improved durability due to calcite re-crystallization and notable change in the chemical composition of potsherd rims which have to be considered when using bulk geochemistry for provenance studies.

Constraining the role of anoxygenic phototrophic Fe(II)-oxidizing bacteria in the deposition of BIFs

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Banded Iron Formations (BIFs) are Precambrian sedimentary deposits of alternating iron oxide and silica mineral layers. Their presence in the rock record ca.3.8-2.2 Ga makes them particularly intriguing formations for the debate over when oxygen became dominant on Earth. The mechanism(s) of BIF deposition is still unclear and suggestions include both abiotic and biotic processes. We are interested in constraining one of these proposed mechanisms; the direct biological oxidation of Fe(II) via anoxygenic Fe(II)-oxidizing photoautotrophs.

In order to find the limitations of photoferrotrophic BIF deposition, we take a holistic approach, investigating the oxidation of Fe(II) by modern Fe(II)-oxidizing phototrophs, the precipitation of Fe(III) (hydr)oxides, and the fate of the cell-mineral aggregates in the water column and at the basin floor.

Specifically, physiology experiments with Fe(II)-oxidizing phototrophs under various conditions of light intensity, pH, Fe(II) concentration and temperature allow us to determine the environmental limits of such organisms. We carry out precipitation experiments to characterize the sedimentation rates, aggregate size and composition in order to resolve the effect of reactions in the water column. Finally, we simulate the diagenetic fate of these aggregates on the basin floor by placing them in gold capsules under temperature and pressure conditions relevant for the Transvaal Supergroup BIFs of South Africa. Recently, we have developed a tank simulating the Archean ocean in which the strains grow in continuous culture and collect the aggregates formed under various geochemical conditions.

We aim to model the extent of and limitations to photoferrotrophs in BIF deposition. This information will help constrain whether biotic processes were dominant in the Archean ocean and will offer insight to the evolution of the early biogeoosphere.
Trace element and Nd-Sr isotope systematics of phonolite and other rocks of the Chico Sill Complex, Northeast New Mexico

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Alkaline igneous rocks of Chico Sill Complex in northeastern New Mexico fall on the trend of the Jemez Lineament, an alignment of igneous centers that obliquely crosses the Rio Grande Rift. These 37 – 20 Ma intrusive rocks are spatially associated with younger rocks of the Raton-Clayton volcanic field, but clearly sample a different source. The sills were emplaced prior to rift extension. A subset of the spectrum of intrusive rocks (including phonolite, phonotephrite, trachyte, and lamprophyre dike rocks) is included in this study.

Phonolite is the most common rock type in the southeastern half of the sill complex and is the product of extreme fractional crystallization of a more mafic parent, but may not have evolved from the other lithologies studied. Trace element ratios and normalized-element plots suggest that at least two distinct differentiation trends produced phonolite, titanite fractionation played a role in differentiation, and a subduction component is absent from the phonolite source but may have contributed to other rock compositions. One odd feature is the enrichment of Zr as compared to other continental alkaline rock suites, in one phonolite trend relative to the other.

The subset of rocks studied shows initial Sr and Nd isotope ratios that are close to bulk-earth values, with epsilon Nd in the narrow range of 2.1 to –1.5 (143Nd/144Nd between 0.51275 and 0.51256), and initial 87Sr/86Sr ratios in the slightly broader, but still clustered range of 0.7042 to 0.7053. These isotope ranges are similar to many ocean-island basalts. The trail of the data toward higher 87Sr/86Sr values suggests a probable mixing curve with granitic or sedimentary rocks of the upper crust, although the degree of contamination must have been small and the contaminant is poorly defined.

Tracing global fallout using $^{210}$Pb and artificial radionuclides inventories in mountainous area

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Inventories of unsupported $^{210}$Pb in soils is used here as a tracer to estimate the effect of parameters such altitude, mean annual rainfall, vegetation on the long term input of atmospheric pollutants over mountainous area. Thus we examine exhaustively the magnitude and extent of soil inventories of unsupported $^{210}$Pb in French mountainous areas. In addition, we combine artificial radionuclides from global fallout (mainly $^{137}$Cs and Plutonium) with $^{210}$Pb to compare deposition mechanisms of artificial and anthropogenic radionuclides. With this view, soils were sampled between 2000 and 2006 along transects of increasing altitude and subsequently increasing annual precipitation rate, in different mountainous areas.

Data shows that $^{210}$Pb soil inventories are coarsely proportional to the mean annual precipitation occurring on each massif. Additionnaly in high-altitude sites, higher $^{210}$Pb inventories than expected are explained by orographic effects. At last, climatic parameters, such as the intensity of rain episodes in Mediterranean regions probably induce specific deposition processes of $^{210}$Pb explaining the relationship observed between soil inventories and rainfall. In addition to altitude and rain amount, the vegetation accounts for the intensity and the extent of $^{210}$Pb deposition, since the excess $^{210}$Pb in woodland soils reaches 30% with respect to grassland.

Although the inventory of $^{137}$Cs and plutonium from atmospheric nuclear weapons in soil also increases with mean annual rainfall, a significant decrease of $^{137}$Cs/$^{210}$Pb ratios is observed in studied massifs from lowland to highland sites. This shows that at least two main tropospheric reservoirs with distinct $^{137}$Cs/$^{210}$Pb ratios contribute to the mountainous soil inventory of atmospheric pollutants.
Extracting sequentially Ra, Nd, Pa, Th and U from a unique natural sample, on the same column

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Multi-proxy approach is very promising for modern and past marine process investigation. However, extracting simultaneously several tracers from the same sample using the same column remains a challenge. Measuring any natural tracer requires sample collection, pre-concentration or mineralization, chemical extraction and spectrometric analysis. Natural concentrations being very low, when each tracer requires its own collection, huge volumes of water have to be taken from the rosette and/or filtered with in-situ pumps, which is time and money consuming. Since the GEOTRACES program objective is to analyse numerous tracers and isotopes along oceanographic sections, there is an urgent need to find ways to analyse as many elements as possible on the same sample. In addition, collecting more samples on the same marine cast will enhance the homogeneity of the final data, and improve the sampling resolution, therefore improving the data set quality.

A new procedure is presented, allowing the simultaneous extraction of 5 tracers (Ra, Nd, Th, Pa and U) from the same natural sample. In addition to isotopic ratios (143Nd/144Nd, 230Th/232Th and 234U/238U) concentrations of 226Ra, 230Th and 231Pa are investigated requiring spike addition, i.e. 228Ra, 229Th and 233Pa / 236U respectively. Accuracy and precision of the analytical methods were evaluated using artificial standards and natural samples (marine suspended particles and rocks). Satisfactory purifications of Th, Pa and U were obtained from this unique column, whereas Nd and Ra extraction require light additional steps.

New productivity in the Eastern Arabian Sea during winter Monsoon

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The biogeochemistry of the Arabian Sea is driven by seasonally reversing southwest and northeast monsoons. Although both the monsoons trigger high primary production, the underlying mechanisms are different. Recent observations on the basis of ocean color studies have shown contradicting trends in ocean productivity for the western and eastern Arabian Sea; it has increased in the western Arabian Sea over last 6 years whereas no such trend is seen in the eastern Arabian Sea [1]. In this context, it would be interesting to know about the export production taking place in this part of the world’s ocean. Measurement of new production using 15N tracer technique [2] provides an avenue to estimate the export production; integrated over an annual time scale new productivity is equal to the export of carbon out of the surface ocean i.e., the export production. We have carried out new productivity measurements in the eastern Arabian Sea during early and late winter monsoon. Our results suggest that during the early winter, though the column N-uptake is low (~8.91mmolN/m²/d) over a large area of the eastern Arabian Sea the f-ratio (new production/total production) is relatively high (~0.66). Results from the late winter, in conjunction with the earlier reported results [3], reveal consistent high column N-uptake rate (~20.1mmol N m⁻² d⁻¹), particularly when the bloom (dominated by heterotrophic Noctiluca Scintillans) develops in the northeastern part. During this period the f-ratio is also very high (~0.86) suggesting enhanced downward transport of newly formed organic matter implying increased sequestration of carbon to the deeper ocean.

References
Stable isotopic trends in Neoproterozoic oceans: A record of global Snowballs, global Slushballs, global methane, global diagenesis, and/or palaeogeography?


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The Neoproterozoic (1000 – 543 Ma) is a period of extraordinary Earth System change marked by extreme climatic fluctuations and hallmark biological innovations (advent of metazoans). Stable isotopic trends (C-O-B) associated with Neoproterozoic marine carbonate rocks display large amplitude fluctuations which many studies have shown are broadly reproducible worldwide and stratigraphically systematic. Amongst the most intriguing of these are from cap carbonates (carbonate rocks which rest directly on glaciogenic rocks, and/or the surface representing palaeo-glacial episodes) which show sharp negative C isotopic excursions (in many localities down to -6‰) followed by recovery to more positive values and concomitant B-isotopic excursions (about 9‰); these have generated lively debate and many studies have been devoted to understanding factors that influenced these excursions. Stable isotopic trends (C-O-B) and δ18O(carbonate) trends can be distinguished based on location and inferred palaeobathymetric position within an individual basin. Along individual craton margins trends are systematic and variations can be reasonably attributed to varying palaeoenvironmental setting, i.e., they are self-consistent and compatible with the geology. However, inter-cratonal comparisons show that stratigraphic (temporal) patterns and amplitudes differ between basins. Although the duration of cap carbonate precipitation remains contentious, it is likely that deposition was relatively rapid (i.e., 10^3-4 years rather than 10^5 years). Our data can be used to imply that the isotopic composition of water masses varied from place to place in Neoproterozoic oceans. This suggests that cap carbonates and their isotopic signatures were a likely product of a dynamic interplay between palaeogeography and palaeooceanic circulation.

Adsorption and dynamics of ions at rutile and cassiterite surfaces

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The interface between aqueous solutions of ions (mostly Rb+, Na+, Sr2+, Cl-, Br-, F-) and metal oxide surfaces, represented by rutile and cassiterite, is studied using molecular dynamics computer simulations. The previously published results for adsorption of these ions at negatively charged surfaces at 25°C are extended to cover higher temperatures up to 150°C and the effect of pH-dependent surface charge density. The effect of the temperature and pH on occupancy of different types of adsorption sites will be compared with predictions of Multi Site Complexation models (MUSIC). The competition between adsorption of several cationic species present in mixed solutions used in titration experiments (e.g. Rb+ and Sr2+) and the adsorption dynamics of ions will be also discussed.

References

No need for involvement of a hidden mantle reservoir in the origin of lamproites from Mediterranean

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Recent discussion about Hf-Nd isotope geochemistry focused on the composition of lamproites and kimberlites as possible evidence for the existence of a hitherto unrecognized ‘hidden’ terrestrial reservoir. This was triggered by the discovery of an apparent discrepancy between terrestrial Hf-Nd isotopes and the BSE chondritic reference value, which could be resolved by the existence of a new geochemical reservoir with Hf-Nd isotopic values below the terrestrial array. Most lamproites do not follow the Hf-Nd array defined by other terrestrial samples, but have variable Nd at almost constant Hf isotopic values. This triggered an attractive hypothesis about their role in the evolution of the Earth and their potential to sample the ‘hidden’ reservoir. Here, we present HF, Sr, Nd and Pb isotope results on Mediterranean lamproites that can be used to further test this possibility.

Mediterranean lamproites are derived from multi-component melts, which combine depleted and enriched end-members(s). The extremely variable radiogenic isotope composition of lamproites points to the importance of mixing between three contrasting geochemical components which appear in 206Pb/204Pb, 87Sr/86Sr and 143Nd/144Nd space: a derivated from the lithospheric mantle and a convecting mantle-most relevant for the deflection of lamproites from the crustal component, an ultra-depleted mantle component of terrestrial Hf-Nd array. Most lamproites do not follow the Hf-Nd array defined by other terrestrial samples, but have variable Nd at almost constant Hf isotopic values. This triggered an attractive hypothesis about their role in the evolution of the Earth and their potential to sample the ‘hidden’ reservoir. Here, we present HF, Sr, Nd and Pb isotope results on Mediterranean lamproites that can be used to further test this possibility.

Mediterranean lamproites are derived from multi-component melts, which combine depleted and enriched end-members(s). The extremely variable radiogenic isotope composition of lamproites points to the importance of mixing between three contrasting geochemical components which appear in 206Pb/204Pb, 87Sr/86Sr and 143Nd/144Nd space: a crustal component, an ultra-depleted mantle component derived from the lithospheric mantle and a convecting mantle-originating component. It is the third component which is the most relevant for the deflection of lamproites from the terrestrial Hf-Nd array.

Our modelling shows that the convective-mantle derived component has high Sr and Nb contents, low HFSE content relative to LREE, significantly higher Nb/Ta and Zr/HF ratios, and lower Zr/Nb and Zr/Ta ratios relative to OIB and chondrite, whereas isotopic compositions are similar to OIB. This geochemical signature is considered as a “hallmark” of mantle carbonatite. In Hf-Nd isotopic space, this component is responsible for the shift of the lamproite values from terrestrial array. We interpret this shift as a mixing hyperbola between carbonatitic melts derived from sublithospheric mantle and lamproitic melts. The deviation from the array is due to the large range in Hf/Nd ratios that vary from up to 0.20 in lamproitic melts to <0.01 in asthenospheric melts, caused by extremely high Zr and HF concentrations in lamproites (up to 1000 and 30 ppm, respectively), and very low HF contents in carbonatitic melts. We discuss a geodynamic scenario which provides a suitable environment for the interaction of coeval asthenosphere-derived and lamproitic melts throughout the Mediterranean region.

REE in the oldest zircons, Okhotsk terrane

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For accurate definition of genetic characteristic of zircons from mafic granulites and gneisses and to find a solution of gneisses and granite-gneisses correlation, REE distribution in zircons had been studied, using SIMS SHRIMP II.

Hyp-Plag granulite schist displays two oldest zircon generations: 1 (3.6-3.7Ga) with volcanic and 2 (3.5Ga) with magmatic inclusions. Volcanic zircons contain max concentrations of REE and (Lu/Sm=104-198, Eu/Eu*=0.2-0.39). Ultra-metamorphic zircons (2) and recrystallized grains (3) contain less REE, especially LREE, REE pattern is steeper (Lu/Sm=370-1305, Eu/Eu*=0.15-0.27).

Some zircons (4) correspond to Proterozoic metamorphic and metasomatic events are represented by altered discordant grains of high U contents and positive Eu anomalies (Lu/Sm=120-129, Eu/Eu* = 2.1-2.9). Its REE concentrations are close to that of zircon 1, but REE pattern for most altered grains is flat (Lu/Sm=40, Eu/Eu*=1.16). Granite-gneisses zircons display two types of REE distribution: for ultrametamorphic cores (3.3Ga) (Lu/Sm=27-117, Eu/Eu*=0.1) and for metamorphic rims (2.7 Ga) (Lu/Sm=165-428, Eu/Eu*=2-0.5). Cores in zircons of granite-host gneisses (3.28 Ga) show REE pattern (Lu/Sm=40-156, Eu/Eu* =0.1-0.2) similar to that for cores of granite-gneisse zircons.

I. Chondritic normalised REE patterns of zircons with volcanic inclusions from Hyp-Plag granulite schist are similar to that of zircons from gabbro (Hoskin, 2000) and correspond to magmatic pattern. It conforms to geochemical data and verifies belonging of such zircons to mafic volcanic protolith.

II. REE patterns of zircons with magmatic inclusions show distribution similar to zircons from leucosome of garnet-free granulites (Rubatto, 2002). III. Cores of zircons from gneisses and granite-gneisses show similar REE patterns, that indicate their origin from common protolith.

References
**Contrasting behaviour of arsenic, iron, manganese and uranium during anaerobic incubation of aquifer sediments from Nadia, West Bengal**

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The critical role of indigenous metal-reducing bacteria in mediating the mobilisation of arsenic from shallow sediments in Bengal has been widely muted, however, there remains debate over the mechanistic details of the mobilisation processes, including the relative importance of enzymatic and abiotic processes. Observing, in suitable microcosm experiments, the behaviour of trace elements with contrasting biogeochemistries might provide some further insight.

Using sediment from 20 m depth from Chakdaha Block, Nadia, West Bengal, we conducted microcosm experiments under anaerobic conditions with 15 g sediment / 30 mL synthetic model Bengali groundwater (after Islam et al., 2004) amended with sodium acetate (as a proxy electron donor) to 0, 0.1, 1 or 10 mM at an initial pH of 7.0, 20°C & 1 atm. Triplicate microcosms were sampled after 1, 3, 7, 10, 14, 22 and 29 days. Trace elements were determined by HR-ICP-MS, As speciation by IC-ICP-QMS, Fe(II) by the UV-Vis based ferrozine method and H\(_2\) by GC-RCD.

Reduction of As(V) to As(III) was observed within 7 days, followed by the mobilisation of As, Fe and Mn and the immobilisation of U mostly within 14 days suggesting increasingly reducing conditions. Release of Mg, Ca, Sr and Ba may be due to dissolution of carbonate phases consistent with increasingly acidic conditions that would be expected. Amendment with acetate made no systematic significant difference to the rate or magnitude of As, Fe or Mn release – this is consistent with large amounts of H\(_2\) generated during the microcosms and the presence of highly reactive organic matter within the sediments. Null results from sterile controls confirmed the overall critical role of microbes. Work is ongoing to characterise the bacterial communities and the nature of the reactive organic components in the sediments.

**Magmatic processes and the evolution of crust: Insights from the New Zealand/Kermadec subduction system**

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It is now well established that andesitic magmas have an ultimate origin in the mantle wedge but the extent to which erupted compositions are modified through crustal interaction is still being defined. Subduction-related volcanic rocks are commonly identified by their textures and by specific trace element characteristics. The textures reflect complex crustal level processes that include assimilation and crystal fractionation (ACF) and magma mixing or mingling. Although commonly interpreted to reflect slab fluid influences, the trace element characteristics are also specific to continental crust. Detailed studies (stratigraphy, major and trace element chemistry, Sr-Nd-Pb isotopes, U-series disequilibria) of andesitic eruptive sequences in New Zealand’s North Island indicate that they represent magmas that evolved through ACF processes operating on variable time scales in complex storage and feeder systems dispersed throughout the crust. Contrasts between individual volcanoes arise because of variations in storage and feeder systems and because, in the more extreme cases, for example Ruapehu and Taranaki, both mantle sources and the crustal assimilants are compositionally different. In the Taupo Volcanic Zone, the principal locus of volcanic activity in the North Island, rhyolitic magmatism marks the onset of rapid extension and high heat flow and is preceded by andesitic volcanism. The change from andesitic to dominantly rhyolitic eruptives reflects progressive thermal evolution of the lithosphere and a shift from mantle and lower crustal dominated genetic and evolutionary processes to those dominated by crustal melting and lower pressure crystal fractionation. These processes occur in both continental and oceanic segments of the New Zealand-Kermadec system demonstrating that it is the thermal evolution of the crust rather than its thickness or composition that controls the mix of lithologies in arc-type volcanoes.
Non-hydrocarbon compounds in oil and gas accumulations: Deep influx constrained by noble gases

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Recent oil and gas exploration demands deeper drilling and more complex targets. It is clear that fluids from a sedimentary basin cannot be considered isolated anymore from deeper fluids (metamorphic zones, continental basement, mantle). This induces negative consequences (occurrence of non hydrocarbon gases contaminating the hydrocarbon accumulations as carbon dioxide and nitrogen) and potential positive ones (high concentrations of helium as an economic resource, possible extra-generation of hydrocarbon gases through non organic processes). Different natural tracers allow us to quantify the importance of such deep fluids contaminants. Among them, the chemical and isotopic compositions of associated noble gases (from helium to xenon) give evidence, according to different oil fields, of mantle contributions from 0 to almost 100%. Very recent direct measurements of lead isotopes confirm that mantle compounds may be associated both as inert gas molecules and heavy metals chemically associated with large organic molecules.

We present two examples of mantle-contaminated petroleum systems, where the noble gas chemical and isotopic patterns indicate a clear mantle contamination. Moreover, an excess of radiogenic 3He is sometimes present, due to a leaching of crustal rocks through the migration of deeper carbon dioxide and/or nitrogen carrier gas, coming from deeper sources. This implies that the usual 3He/4He ratio, used commonly as an indicator of mantle contamination, may be useless, whereas the use of 3He, associated with other gases (CH4, CO2, N2, etc...), indicates clearly a mantle signature for deeper sources. This implies that the usual 3He/4He ratio, used commonly as an indicator of mantle contamination, may be useless, whereas the use of 3He, associated with other gases (CH4, CO2, N2, etc...), indicates clearly a mantle signature for deeper sources.

Non-hydrocarbon compounds in oil and gas accumulations: Deep influx constrained by noble gases

U-Th-Ra fractionation in soil horizons of forested ecosystem (Strengbach catchment, France)

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The 238U series nuclides (238U, 234U, 230Th and 226Ra) are recognized as tracers and chronometers of weathering processes. Using these tracers requires to understand the parameters and processes controlling their fractionation in soils surface horizons. In order to constrain these processes, the different compartments (soil profile, soil solutions and vegetation : wood, leaves, branches and roots of beeches) of a experimental plot, situated in the Strengbach catchment (OHGE http://ohge.u-strasbg.fr, Vosges, France) have been sampled and analysed for major-trace elements and U-Th-Ra isotopes.

The shallower horizons of the soils have highest (226Ra/230Th) and lowest (230Th/234 U) activity ratios (a.r.), respectively 1.41 and 1.12 compared to the other horizons of the soil profile. The analytical data of the different compartments of the vegetation suggest that the plants are characterized by very high (226Ra/230Th) ranging from 20 to 164 and low (230Th/234 U) ranging from 0.84 to 0.97. Based on these results, we suggest that the geochemical signatures of the soils surface horizons (-40 cm) are influenced by litter recycling which could provide 226Ra and 234U excess in these horizons.

The (226Ra/238U) a.r. of the soil solutions (1.88-4.75) are higher than most of the corresponding soils (~ 1.5). They decrease from the top of the profile to 30 cm depth and then increase weakly until 60 cm depth. The vegetation, which is responsible of both the litter recycling and the root uptake displays very high (226Ra/238U) ranging from 100 to 300. We propose that litter recycling influences the isotopic characteristics of the shallower soil solutions. The fractionation induced by root uptake, which mainly operate between 30 and 40 cm depth, could explain the lower (226Ra/238U) in soil solutions at these depths.

Therefore U series disequilibria allow to constrain the dynamics of a soil system. Moreover, the data point to the important role of the vegetation in controlling the geochemical/isotopic signatures of the soils surface horizons and soil solutions (-30 cm) by litter recycling and root uptake.

Reference

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Titanium oxide in ocean island basalts (OIB) and the preservation of extreme isotopic signatures

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We have examined liquid lines of descent for a large set of ocean island basalts (OIB) using a compilation of major element data from the GEOROC database. We focus on the moderately incompatible element titanium and identify a ‘reference’ TiO2 value for each OIB to reflect approximate primitive lava compositions before significant fractional crystallization or crystal accumulation. High reference values are observed in OIB with low inferred degrees of melt lying above thick lithosphere, whereas low reference values are seen in OIB with larger inferred degrees of melt, atop thinner lithosphere. We find that the reference abundances are in most cases too high to be produced by melting of any plausible peridotitic mantle composition. Therefore, an additional Ti-rich component is required in the source of virtually all OIB. Recycled mafic crust appears to be the most geochemically consistent source for the extra Ti.

The OIB we investigated cover the full range of radiogenic isotopic mantle endmembers. Notably, OIB with low reference TiO2 values plot in restricted, depleted ranges in Sr-Nd isotopic space, whereas OIB with higher reference TiO2 values exhibit enriched isotopic signatures and expansive ranges in Sr and Nd isotopic ratios. Since higher reference TiO2 values likely result from smaller degrees of melting, they may preserve extreme isotopic ratios. Larger degrees of melting may dilute enriched isotopic signatures. Therefore, degree of melting in OIB may be a dominant control on both the observed range of isotopic ratios and the ability to preserve extreme signatures. However, recycled crust does not generally produce extreme isotopic signatures seen in endmembers such as EMI and EMII, making other components necessary to explain the full breadth of isotopic data.

Platinum-reaction-oxygen and HSE systematics of Belingwe komatiites

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Studies of the origin and evolution of the relative and absolute abundances of the highly siderophile elements (HSE) in the mantle provide information regarding the late accretionary history of the Earth, oceanic crustal recycling, timing of melt extraction from the mantle, and possibly the mechanisms and the extent of core-mantle exchange. We present high-precision data for HSE abundances and Pt-Re-Os isotope systematics for twenty drill-core whole-rock samples and olivine and chromite separates from the ~10-m thick Tony's komatiite flow, which is among the freshest Archean komatiites on Earth. The emplaced lava contained 24% MgO, was depleted in LILE and had εNd(T) = +2.5. Re-Os data for two whole-rock samples and corresponding mineral separates define an internal isochron with an age of 2686±11 Ma and a γ187Os(T) = 0.13±0.08. Regression of the data for all samples yields an isochron with an age of 2674±44 Ma and a γ187Os(T) = -0.22±0.48. A single B2 sample analyzed for Pt-Os has an initial 186Os/188Os = 0.1198324±13, which is identical to the initial 186Os/188Os = 0.1198322±8 determined earlier for the contemporary Pyke Hill komatiite source. Both sources have similar ε186Os(T) = 0.05±0.11 and 0.05±0.07, respectively, relative to the bulk solar system initial 186Os/188Os = 0.1198269. The Belingwe source, thus, evolved with long-term 186Re/188Os = 0.400±4 and Pt/Os = 1.7±0.2, which are indistinguishable from those in chondritic meteorites. The IPGEs (Os, Ir, Ru) in the whole-rock samples are strongly positively correlated with MgO identifying the Belingwe komatiite as belonging to the Munro-type flows. The PPGEs (Pd, Pt) and Re show strong negative correlations with MgO, coincident with olivine-control lines. The HSE composition of the Belingwe source was calculated from the regressions of HSE abundance data vs. MgO for the whole-rock samples and the Pt-Re-Os isotopic data. The source contained (ppb): Re 0.23, Os 2.6, Ir 2.3, Ru 5.2, and Pt and Pd 4.3. The Ru/Ir = 2.3±0.3 and Pd/Ir = 1.9±0.2 in this source are higher than those in any known groups of chondrites, but match the recent estimates for the Earth’s primitive upper mantle derived from analyses of mantle xenoliths worldwide, or the recently obtained HSE data for some lunar impact melt breccias “fingerprinting” the composition of late accreted materials to the Moon and the Earth. The new data provide further constraints on the evolution of PUM in the Archean and stimulate additional studies of the composition of materials added to the silicate Earth in the form of the “late veneer”, as well as chondritic meteorites.
Noble gases composition of palaeo Archaean atmosphere and mantle

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Several models of the noble gas evolution of the Archaean atmosphere-mantle exist [1, 2, 3], with implications on our understanding of the development of the early Earth and the appearance of life.

Pristine drill core samples (Pilbara Drilling Project) from the 3.525 Ga chert-barite of the Dresser Formation (North Pole, Western Australia) allowed fresh samples preserving primary fluid inclusions unaffected by surface weathering to be directly analysed using synchrotron and mass spectrometer methods. The Dresser formation has been interpreted as a shallow basin strongly affected by hydrothermalism practically during formation of the basin and prior to early diageneis [4, 5]. This chronology permitted primary fluids from different origins (marine, hydrothermal) to be trapped within the volcano-sedimentary sequence.

Two studies, one of intrapillow quartz pods overlying chert-barite deposits [6], and the other of the same formation but 100 m deeper, have been carried out. Synchrotron X-ray microfluorescence shows the presence of three fluid endmembers (in different proportions) in fluid inclusions in quartz. Two of them, enriched in Ba and/or Fe, are likely to originate from the hydrothermalism while the third, metal-depleted, fluid is the North Pole seawater endmember. Primary fluid inclusions from the bottom of the Dresser formation are dominated by hydrothermal fluids, which allow us to constrain the noble gases hydrothermal signature.

Inclusion-trapped fluids were analysed by mass spectrometry (using a Helix Multicollector) following extraction of the fluids by in vacuo crushing. Neon isotopes, 36Ar and 40Ar, 84Kr, 129Xe, 132Xe and 136Xe were measured in fluid inclusions and in the host matrix. The results show mixing between two fluids, confirming previous studies. The Seawater pole reveals the composition of the palaeo atmosphere thus it is possible to determine the composition of palaeo archaean mantle within the signature of hydrothermal fluid.

References

Constaining groundwater residence times in a fractured aquifer using noble gas isotopes

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In fractured rock aquifers, groundwater ages obtained with environmental tracers usually do not represent the hydraulic age of the water. Solutes in the water have diffusive access to the micro pores of the rock matrix and are therefore retarded compared to the water flux in the fractures. In a system of parallel fissures, the ratio between the apparent tracer age and the water age depends on the extent of diffusive penetration between the fractures and the matrix. Visa versa is the penetration depth in transient conditions a function of the groundwater residence time in the fractures (Maloszewski and Zuber, 1994). This intrinsic dilemma for groundwater dating can only be reduced by the use of multiple tracers with different decay constants and input histories. In the present study 85Kr (T1/2: 10.76 yr, 39Ar (T1/2: 269 yr) and 14C (T1/2: 5730 years) were used in order to constrain the groundwater residence times in a fractured aquifer in the Clare Valley Australia (Love et al., 1999). In the atmosphere 39Ar is mainly produced by cosmic ray induced Ar(n,2n)39Ar reactions. In this study the subsurface secular equilibrium 39Ar activity due to the 39K(n,p)39Ar reaction exceeds the atmospheric value of 1.8 mBq/L Argon (Loosli, 1983) by a factor of two. The subsurface ingrowth rate can, however, be interpreted in terms of groundwater residence time. The obtained time scales support findings from indicators of past recharge conditions. (Love and Herczeg, 2001).

References
U and Th deficit in primitive mantle xenoliths and the nature of core power activity

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The goal of this study was to check the hypothesis according to which the core energy activity is due to radioactive decay of U and Th contained in the core. The idea of such checking consisted in the following: to identify xenoliths of the geochemically closed primitive mantle (PM) material, to determine concentration of U and Th in them and using balance calculation to estimate the content of these elements in the core which is a complementary reservoir to the PM. Original analytical data for 53 mantle xenoliths together with the numerous published data were analyzed. The material of geochemically closed PM was identified on the basis of MREE and HREE concentration, Al/Mg, Ca/Al, Mg/Si, Sr/Mg ratios and isotope composition of Pb and Os. Concentration of U (13-36 ppb) and Th (37-59 ppb) in such material is similar to that in chondrites, but lower than concentration of these elements, which would take place in silicate shell formed from chondrites after segregation of the core devoid of U and Th content. This deficiency is most distinctly apparent if to compare the U and Th concentration observed in the PM xenoliths with that in the silicate shell produced from CV-chondrites. All this allows us to assume that deficient elements of the primitive mantle are located in the liquid core complementary to it. The balance calculation showed that, according to the results obtained, the U concentration in the core corresponds to 19 ppb at initial concentration of uranium for Bulk Earth like that in C1 and 25 ppb at this initial concentration like that in CV. According to the calculations [1], such U content is high enough to generate a thermal energy from 3 up to 4.5 TW out of 7 TW attributed to the core. Taking into account that the estimated U and Th concentration in the core corresponds to the minimal value (because their content in the PM may be overestimated due to some contamination of xenoliths by hosted basalt) the hypothesis of the core power activity generated by radioactive decay of U and Th looks valid.

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Reference

A mechanism of fluid transport through minerals

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Previous explanations for the movement of aqueous fluids through rocks have concentrated on the availability of pre-existing pathways, such as grain boundaries and stress fractures (Kostenko et al., 2002). Such pathways undoubtedly play a major role in allowing easy access for fluid transport. However, there is a lot of evidence that fluids migrate through minerals, which are reactive in the presence of an interfacial fluid layer (Putnis et al., 2005; Putnis and Putnis, 2007). Using time-lapse photography, fluid movement through a single crystal of a simple salt is observed at room T and P and presents a model for more complex mineral systems, showing similar textural and compositional equilibration features. The pseudomorphic replacement of one phase by another is characterised by the development of porosity in the product phase. This porosity provides the pathway for mass transport through the parent phase, which is replaced by the product at a moving interface within the mineral during an interface-coupled dissolution-reprecipitation replacement process. Replacement textures commonly occur in relation to fluid-driven regional metamorphism and large scale metasomatism e.g the gabbro - to eclogite facies transition, western Norway (John et al., 2007), serpentinization and rodingitization of the oceanic lithosphere and scapolitization of gabbro (Austreheim et al., 2007), suggesting that dissolution-reprecipitation is an important mechanism behind large-scale metamorphic and metasomatic processes.

References
Global volcanic emissions of SO$_2$, halogens and trace metals, 1998 - 2005

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We have quantified annualised global volcanic emission rates based on a compilation of measurements at 60 active volcanoes, for the years 1998 – 2005. The global mean emission rate is 16 Tg SO$_2$/yr, of which 9 Tg/yr (56%) is emitted by non-explosive activity. Corresponding mean annualised halogen emissions are ca. 4 Tg HCl/yr; 0.3 Tg HF/yr and 0.6 Tg HBr/yr.

There is, as expected, a large interannual variability, with measured global volcanogenic SO$_2$ emissions varying between 13.3 Tg/yr in 1998 to 21.3 Tg/yr in 2000; most of this variability was due to sustained emissions from two persistently degassing volcanoes (Popocatepetl and Miyakejima). There were no major explosive eruptive sources (no eruptions of VEI 5 or larger; 1 eruption of VEI 4) during this period. Extrapolation to account for the un-measured emissions at a further 58 active volcanoes may extend the annual average SO$_2$ emission rate to ca. 20 Tg SO$_2$/yr for the period 1998-2005.

Using this global volcanic sulphur emissions inventory as a basis, and combined with appropriate field measurements, we can now extend the analysis to make well constrained projections of the fluxes of other important volatiles (H$_2$O, CO$_2$); volcanic nano-particles, and volatile trace metals (e.g. Hg) to the troposphere, and thereby evaluate the importance of persistent volcanic degassing to global geochemical budgets. Considerable uncertainty remains over the trace gas and trace metal emissions to the stratosphere associated with explosive volcanic eruptions, due to a lack of appropriate measurements.

Geochemistry and genesis of the Qibaoshan gold-copper deposit in Shandong Province, eastern China

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The Qibaoshan is a medium-sized Cu-Au deposit located in a caldera near the east of Yishu deep fault zone. This deposit consists of two parts, the upper part is a gold-containing breccia pipe, and the lower part is a copper-bearing stockwork.

The caldera covers an area of 10-12 km$^2$ and rocks around it are distributed in ring shape. The inner ring consists of subvolcanics, such as pyroxene monzonite, quartz monzonite porphyry, and trachyandesite porphyry; the outer ring comprises predominantly of trachyte, trachyandesite and minor rhyolite. In southeast of the central intrusive body, there is a cryptoexplosive breccia pipe which develops gold and copper mineralization.

Mineral association of this deposit displays a clear vertical zoning, i. e., from 0 to -20 m, the dominant mineral is gold-bearing specularite; main minerals are commonly specularite, manganosiderite, quartz and minor amounts of pyrite and chalcopyrite from -20 to -70 m; and pyrite and chalcopyrite from -70 to -120 m. Wall-rock alteration is widespread in the ore district. Main alteration types are phyllic alteration, silicification and carbonatization, and in the deep part of the pipe there also develops potassic alteration.

Fluid inclusion studies show that the homogenization temperatures range predominantly from 250°C to 350°C. The estimated salinities of ore-forming fluids vary between 10.6 and 32.6 wt% equiv. NaCl. The main compositions of ore-forming solutions are characterized by enriched in Ca$^{2+}$, Na$^+$, Cl$^-$ and depleted in Mg$^{2+}$, K$^+$, F$^–$. The F$/\text{Cl}^–$ ratios of hydrothermal fluids increased obviously from the main mineralization stage to late mineralization stage, indicating that the ore materials were transported predominantly as chloride complexes.

The $\delta^{18}$O$_{H_2O}$ values of ore-forming fluids during main mineralization stage range from 3.05‰ to 5.77‰, and $\delta$D$_{H_2O}$ from –78.6‰ to –48.1‰. In late mineralization stage, the $\delta^{18}$O$_{H_2O}$ and $\delta$D$_{H_2O}$ values are –7.77‰ and –73.4‰ respectively, indicating a major meteoric water component. The $\delta^{34}$S values of sulfides vary between 0.30‰ and 3.59‰, with a $\delta^{34}$S$_{2\text{SS}}$ value of 2.80‰. Overall, the H, O and S isotopic data suggest that the ore-forming fluids and materials might be originated mainly from magmatic source.

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