

Various epithermal precious metal systems in the Urumieh-Dokhtar magmatic assemblage, Iran

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The Urumieh-Dokhtar magmatic assemblage (UDMA) in west-central Iran is dominated by Cenozoic calc-alkaline volcanic, pyroclastic and shallow intrusive rocks. The development of UDMA is related to the evolution of the Neotethys in western Asia. The UDMA hosts numerous Cu±Mo±Au porphyry systems, including the world class Sarcheshmeh and Sungun. Several epithermal gold systems are recently discovered in northern UDMA, represented by Masjed-Daghi (MD), Sharafabad (SA), Zaglic (ZL) and Safikhanloo (SK) prospects. Mineralization is restricted to silica, silica-carbonate and silica-barite veins. Pyrite is the main sulfide, associated with minor chalcopyrite, sphalerite and galena. Gold occurs as fine particles in silica and in sulfides. The country rocks are medium- to high-K calc-alkaline and alkaline volcanic-pyroclastic rocks of dominantly andesitic composition with features typical of continental magmatic arcs. Alteration minerals vary from chlorite-carbonate-montmorillonite in SK and ZL, to kaolinite-illite in SA and alunite-kaolinite in MD. Fluid inclusions show a wide range of T_H (120-350°C) and salinity (<1-15 wt% NaCl equiv) (Alirezai *et al.*, 2008, ACROFI-2, Kharagpur, India). A positive correlation exists between the salinity of the fluids and the base metal contents in the veins.

Considering the alteration assemblages, vein minerals and FI data, the epithermal systems vary from low-sulfidation (ZL and SK) to intermediate-sulfidation (SA) and high-sulfidation (MD). Sulfur isotope values for sulfides display a shift in $\delta^{34}S$ from around 0‰ in MD (1.2 to -1.1‰) to increasingly more negative values in SA (1.7 to -6.9‰) and ZL and SK (-2.9 to -7.6‰). The $\delta^{34}S$ values suggest a decreasing role for magmatic fluids, or increasing water/rock interaction, from HS- to IS- and LS- epithermal systems. This is consistent with the chemical and physical characteristics of the fluids involved in the formation of the epithermal gold systems.

Characterization of chemistry and microbial community in Lake Tranebärssjön - A former uranium open pit mine

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Aim, Site Description and Sampling

The aim of this study was to investigate the connection between biogeochemical functions and bacterial community composition in lakes with the focus on the consequences for metal mobilisation and transport in mining areas.

As a study site Lake Tranebärssjön, the former open-pit mine in the closed uranium mine at Ranstad, Sweden was chosen.

The lake was sampled at stratified conditions in late summer at the deepest part of the lake at three depths of the water column; surface water, thermocline and bottom water. Samples were analysed for chemistry, dissolved organic carbon and metals. The bacterial communities of the samples were monitored by 454-pyrosequencing of 16SrRNA genes.

Results and Discussion

The oxygenated surface and thermocline water show pH 7.8 compared to 7 in the oxygen depleted bottom water. The conductivity, alkalinity and the sulfate as well as several metals including Fe, U, Mn, Mo and Ni show higher levels in the oxygen depleted bottom water compared to the oxygenated surface water.

As a result of the strong stratification in Lake Tranebärssjön precipitations of iron hydroxides with associated metals is deposited on the lake shores at spring and autumn turn over. Other studies have implicated that this could be partly caused by microbial reduction in the bottom water of the lake.

Several studies have shown that the geochemical environment controls the microbial populations but also that the microbes can control or influence the geochemistry of elements. We hope that the results from the bacterial community analysis will shed more light on this and contribute to the understanding of the connections between geochemistry and microbial community in this environment.

Springtime boreal VOCs: The role of monoterpenes in selected intense nucleation events (source inventory)

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Boreal coniferous forests have been shown to profoundly influence regional atmospheric chemistry through the emission of reactive trace gases such as monoterpenes and their oxidation products. The role of these organics in new particle formation has been the subject of considerable research activity in recent years, but is not fully understood. The composition of newly formed ultrafine atmospheric aerosols is not known with certainty. A small number of field studies on newly formed particles (3–5 nm) have concluded that they were primarily composed of high molecular weight oxidised organic species. However, sulphate/organic mixtures have also been suggested.

In this study we present measurements of trace gases and aerosol made in a boreal forest during the BACCI-QUEST IV intensive field campaign in Hyttälä, Finland in April 2005. Several clear aerosol events were observed and some of these events are synchronized with huge increases in monoterpenes, while others seemed to correlate more strongly with sulphuric acid. Here we elucidate these two distinct forms of aerosol production at the Hyttälä using the data from the measurements, the information from the back trajectories of air masses and optical stereoisomery of monoterpenes.

Radiogenic isotope signatures of clay-size sediments in the Eastern Indian Ocean: Weathering inputs and current regimes during the latest quaternary

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The terrigenous sediments along the Indonesian and western Australian shelves either originate from the Indonesian islands, which are mainly characterised by young volcanics, or from western Australia, which consists of old, Archaean to Proterozoic rocks. The geochemical composition of the terrigenous shelf sediments is directly linked to erosion and weathering of rocks in the hinterland. This detrital material is advected by the local currents and gets deposited at various distances from its origin as a function of grain size.

Analyses of the radiogenic Nd, Sr, and Pb isotope ratios on the terrigenous clay size fraction of eastern Indian Ocean sediments allow the distinction of three different source provinces: Northern and Central Sumatra, the Java-Banda Province, and northwestern Australia. All isotope systems show a large range in isotopic composition, as well as a high spatial variability. Nd (Sr) isotope compositions range from $\epsilon_{\text{Nd}} = -21.5$ (0.8299) off the northwest Australian coast to $\epsilon_{\text{Nd}} = +0.7$ (0.7069) in samples southwest of Java. Pb isotope compositions also show a very large variability between 17.44 and 19.89 in $^{206}\text{Pb}/^{204}\text{Pb}$ and between 0.7962 and 0.8916 in $^{207}\text{Pb}/^{206}\text{Pb}$.

Two cores, FR10/95-GC5 and FR10/95-GC17, located under the present pathway of the Indonesian Throughflow (ITF) and the Leeuwin Current (LC), respectively, recorded changes in sediment transport and provenance related to ocean circulation and weathering inputs during the latest Quaternary. The radiogenic isotope records indicate that the area north of 18°S was relatively stable during the last glacial and interglacial, and was mainly affected by the eastward flowing South Java Current. In contrast, the area south of 18°S experienced major changes in isotope composition of the clay size minerals: The intensity of the ITF was greatly reduced and the LC was absent at the location of the core during the last glacial, while the West Australian Current was stronger and showed a larger extension.

Search for organics and life on Mars

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Mars lies at the frontier of planetary science and the question of whether life arose on Mars has been widely debated. A combination of energetic ultraviolet radiation, the extreme dryness and the presumed oxidizing nature of the soil make Mars' present surface an inhospitable place for terrestrial organisms. However, conditions in the early history of Mars including a denser atmosphere and persistent liquid water at the surface may have been more favourable for life in the past. Also there is new evidence for a geological history in some areas of volcanic or periglacial activity as shown by Mars Express and Mars Reconnaissance Orbiter. We may expect to find remnants of extinct life or eventually extant life in subsurface environments. Even without an active ecosystem on Mars the surface should not be totally devoid of organic carbon. Meteoritic infall ought to result in measurable levels of carbon compounds in the surface regolith. Apart from organic molecules, minerals may preserve evidence of the former presence of life processes over long time-scales. In order to support future endeavours to search for life on Mars we have to understand the processes that may alter organic matter on the martian surface, how we can distinguish biologic from abiologic organic matter and how we can trace the influence of microbial catalysis. A strategic search for life on Mars needs a thorough interdisciplinary preparation phase that includes Mars laboratory simulations, computational studies, extensive terrestrial field tests at Mars analog sites such as the Atacama desert and Mars Desert Research Stations. We discuss *in situ* instrument development focussed on the future identification of organics and biosignatures on Mars. We shall review the perspectives for life detection and characterisation of organics on Mars, using advanced instrumentation for ExoMars and future Mars missions.

Behaviour of As in sequential sediment extractions observed by μ Sy-XRF analysis

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Naturally As contaminated groundwaters frequently occur around the world and pose a serious threat on human health. The concentration of dissolved As in aquifers, however, is not necessarily determined by the levels of As in the ambient sediment but rather by the type of fixation. Knowledge of the preferential associations and the fixation of As is often gained by means of sequential extractions. These methods are easy to use but they do not provide information where and how exactly As is bound within a mineral grain. Furthermore, little is known about possible geochemical changes that actually occur within a grain during sequential extraction. Therefore, μ Sy-XRF was applied to study the micro-scale distribution of As and other elements in sediments from an As-burdened aquifer of the Red River Delta, Vietnam. The sediments were sequentially extracted following the scheme of Keon *et al.* [1].

In the untreated samples, elevated As concentrations were detected in Fe bearing phyllosilicates (<60 ppm), sulphides (<140 ppm) and Fe oxy-hydroxide coatings (<140 ppm). In the coatings, As is positively correlated with Fe and other heavy metals like Zn, Cu, Mn or Ni. The distribution of As within distinct mineral phases often showed very heterogeneous patterns. Samples which released high fractions of As during phosphate leaching still showed distinct Fe coatings on the sediment particles. The release of As in this leaching step was also evident from the disappearance of correlation between As and Fe as well as from a higher Fe/As ratio compared to untreated samples. The Fe oxy-hydroxide coatings were dissolved to a large extent during subsequent extraction steps. Preferential release of Fe compared to As during this Fe leaching steps was indicated by lower Fe/As ratios compared to the untreated samples. The correlation between As and Fe was preserved only in association with K, indicating the presence of both elements in silicate structures. It can be concluded that μ Sy-XRF analysis is suitable to better understand the effect of sequential extractions on sediments.

[1] Keon *et al.* (2001) *Environ. Sci. Technol.* **35**, 2778-2784.

New capabilities for small-scale and high-precision SIMS analyses

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Secondary ion mass spectrometry (SIMS) has wide application for *in situ* geochronology, trace element and isotope analysis. Despite the strengths of SIMS techniques, their usefulness has been limited for many problems by the relatively coarse scale of analysis (~10-30 μm), and poor precision for element abundance ratios (~1-10 %, relative). Three recent innovations in SIMS instrumentation have improved capabilities in both regards, creating opportunities for new kinds of applications: (1) The NanoSIMS provides a reduced primary beam size (typically 100-300 nm; as small as 10's of nm). A conventional SIMS instrument equipped with a Gallium source can achieve similar resolutions, though at the cost of significantly reduced sensitivity. (2) The NanoSIMS is also the first ion microprobe capable of simultaneous detection of elements differing greatly in mass (up to a factor of 22; e.g., ¹²C and ²³⁸U). This allows for multi-collection of most element ratios, much as isotope ratio multi-collection is done on lower-dispersion mass spectrometers. (3) The ims-7f Geo provides a 'pseudo multi-collection' capability. This is intended as a poor-man's instrument for high-precision isotope ratio analysis, but also permits element ratio measurements at greater than normal speed and precision.

We will illustrate the limits and uses of these new capabilities, focusing on applications to problems in earth science, including petrology, fossilized and recent bio-materials, and geochronology. External errors for major and trace element ratios measured by multi-collection and 'pseudo multi-collection' are demonstrably controlled by counting statistics across a wide range in concentration and down to ~ $\pm 2-3$ per mil precision. This capability exceeds those of e-beam methods in several respects and enables a variety of new applications to paleoclimatology, geothermometry and 'geospeedometry'. For example, we will demonstrate how NanoSIMS images can be used to characterize diffusion gradients of minor elements between adjacent phases in metamorphic rocks, with spatial resolution an order of magnitude smaller than the e-probe and sensitivity sufficient to measure concentrations below the detection limits of ATEM. Finally, we will discuss limits of U-Pb geochronology at μm and smaller scales through processing of NanoSIMS ion images.

Non-equilibrium stable isotope partitioning in igneous processes?

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Studies of the stable isotope compositions of igneous rocks commonly assume that crystallization occurs under conditions of melt/solid equilibrium and that disequilibrium fractionations, when observed, reflect mixing processes. However, igneous phenocrysts commonly exhibit oscillatory, sector, and more complex zoning of major and trace elements that could be produced by diffusion-limited transport near the crystal/melt interface and/or by partitioning into structurally anomalous surface sites. And, melt-phase inter-diffusion is known to lead to gradients in stable isotope compositions. We look for evidence that stable isotope compositions of phenocrysts could reflect such disequilibrium during growth.

We made 255 ion probe (IMS-1280) measurements of $\delta^{18}\text{O}$ in 35 magmatic and mantle olivines and pyroxenes from 5 hand samples of diverse igneous environments and compared $\delta^{18}\text{O}$ to zonation in other elements (especially P; analyzed by EMPA and NanoSIMS). 29 of the 35 studied grains are homogeneous in $\delta^{18}\text{O}$ within the ± 0.2 ‰ analytical precision. This population includes grains with oscillatory μm -scale P banding. Their lack of $\delta^{18}\text{O}$ variations suggest that whatever factors lead to this common mode of trace element zonation have no detectable effect on melt/crystal partitioning of oxygen isotopes. Large (2‰) oxygen isotope variations are observed in one olivine glomerocryst from Mauna Kea, Hawaii. This glomerocryst contains skeletal and equant P-rich domains, and these P-rich domains are systematically low in $\delta^{18}\text{O}$ compared to adjacent, later-grown, P-poor olivine. This trend appears to contrast with previous measurements showing decreasing $\delta^{18}\text{O}$ with decreasing Mg# in Mauna Kea olivines that have been attributed to AFC processes. The unusual oxygen isotope zonation pattern we observe might reflect a kinetic fractionation during nucleation and growth of the cores of some olivine phenocrysts (e.g., if diffusion-limited growth 'feeds' the crystal surface with components that are lower in $\delta^{18}\text{O}$ than equilibrium with bulk co-existing melt.) Alternatively, these data might reflect addition of a low $\delta^{18}\text{O}$, P-rich component to some Hawaiian magmas just before nucleation of olivine. We are testing the first of these hypotheses by measuring $\delta^{18}\text{O}$ distributions in synthetic olivines grown at a range of rates and exhibiting diverse patterns of P enrichment.

'Clumped isotope' thermometry for high-temperature problems

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Paleothermometers for shallow-crustal environments ($50 \leq T \leq 300^\circ\text{C}$) are generally empirical, semi-quantitative, or depend on knowledge of the compositions of pore-fluids. Carbonate clumped isotope thermometry (i.e., paleotemperature estimates based on ordering of ^{13}C and ^{18}O in solid carbonate minerals) potentially provides a means for quantitative, thermodynamically-based temperature estimates in shallow crustal environments, independent of knowledge of or assumptions regarding compositions of co-existing fluids. Application of clumped isotope thermometry at high-temperatures faces several hurdles: limits to precision; relevant calibrations; and preservation (i.e., 'blocking temperature').

Analyses of synthetic and natural calcite and dolomite suggest that both conform to a single continuous relationship between temperature and extent of ^{13}C - ^{18}O ordering between 0 and 1100°C . These data extend previous findings that a wide variety of biogenic and a-biogenic calcites, aragonites and carbonate-apatites approximately follow a single temperature dependent calibration of the carbonate clumped isotope thermometer. However, the temperature dependence is not precisely linear in dimensions of Δ_{47} vs. T , T^{-1} or T^{-2} . The actual T -dependence resembles but is not identical to that predicted by first-principles theory. Minimum analytical errors in T are $\sim 1\text{-}2^\circ$ below 50°C , 3° at 100°C , 5° at 160°C and 10° at 270°C . Routine errors are $\sim 2\times$ greater.

Apparent temperatures of calcites from slowly cooled marbles suggest a 'blocking temperature' of $\sim 200^\circ\text{C}$. This is consistent with studies of a variety of shallow-crustal rocks, which preserve a range of apparent temperatures that seem to be dictated by their extents and conditions of recrystallization. Experimental investigations of the kinetics of ^{13}C - ^{18}O ordering in calcite are consistent with this conclusion, but reveal unexpected evidence for a first-order intracrystalline isotope exchange reaction that leads to partial re-equilibration at $\leq 350^\circ\text{C}$.

This tool will be useful for a variety of problems involving crustal rocks from depths of $\leq 8\text{-}10$ km, including: fault friction, subduction geotherms, origins of blueschists, hydrothermal systems, Buchan metamorphism, basin thermal histories, oil, gas and coal genesis, and fossil extremophiles.

Sulfur cycling in contaminated subsurface ecosystems: Linking stable isotopes to microbial ecology

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Over the past 50 years an increased anthropogenic input has altered groundwater quality. The microbial degradation of contaminants is the only sustainable mechanism of self-purification of contaminated groundwater systems. However these processes, particularly the controls, are poorly understood and an improved understanding is necessary in order to save groundwater as future drinking water resource. In this study we focused our work on the biogeochemistry of sulfur and hypothesized that sulfur cycling is a driving factor in the degradation of contaminants in subsurface ecosystems. We have characterized groundwater sulfate, hydrogen sulfide, sulfite and elemental sulfur across a high resolution depth profile across a fair oil contaminated aquifer at a former gas worksite. Furthermore, we linked our results to the aquifer microbial community patterns to identify the complex sulfur cycle in the subsurface ecosystem. The isotope data in the $\delta^{18}\text{O}$ of groundwater sulfate suggest that in the uppermost few centimeters of the saturated zone, which is characterized by elevated hydrogen sulfide and sulfite concentrations, sulfur cycling proceeds mostly via the reaction of reduced sulfur species with oxygen, with the latter stemming from the overlying unsaturated zone. Underneath the plume core, a region characterized by a strong decrease in contaminant concentrations and elevated $\delta^{34}\text{S}$ values in groundwater sulfate, hydrogen sulfide may be oxidized by Fe(III) minerals to elemental sulfur, and to a lesser extent to sulfite. By coupling the microbial community distribution to $\delta^{34}\text{S}$ fingerprints in groundwater sulfate and hydrogen sulfide we found clear evidence that elemental sulfur is repeatedly reduced to hydrogen sulfide which may be accompanied by the oxidation of organic contaminants, followed by the oxidation of the reduced sulfur species to elemental sulfur by Fe(III) minerals.

What causes the positive feedback between climate and chemical weathering rates?

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Recent fieldwork has demonstrated a strong climate dependence of the chemical weathering rates of eight nearly pristine basaltic river catchments in NE-Iceland [1]. This positive feedback plays an essential role in moderating global climate over geological timescales. Climate may influence chemical weathering rates via two different processes: changing temperature and changing run-off. The goal of this study is to determine the relative influence of these two factors in controlling the feedback between climate and weathering.

Chemical weathering is controlled to a large extent by mineral dissolution. Experimental studies demonstrate that the basaltic glass and Al-silicate mineral dissolution rates are influenced by; 1) an activation energy through the Arrhenius term, 2) the concentration of activated surface sites through surface proton – aluminium exchange reaction, and 3) the saturation state of the dissolving glass [2]. Water samples collected from NE-Iceland was used together with an experimentally generated dissolution rate equation [2] to analyse the effect of temperature and runoff on each of the three factors influencing dissolution. Runoff is found to only influence rates via the solution saturation state, but for the most part this influence is minor due to the strong undersaturation of the natural waters with respect to basaltic minerals. These results suggest that temperature rather than run-off dominates the feedback between climate and chemical weathering in basaltic terrains, and thus may be the most critical parameter controlling CO₂ moderation on a global scale.

[1] Gislason *et al.* (2009) *Earth Planet. Let.* **277**, 213-222.

[2] Gislason & Oelkers (2003) *GCA* **67**, 3817-3832.

Along-arc variations in the Aegean: contrasting Aegina-Methana-Poros, Santorini and Nisyros

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The volcanic islands of Aegina-Methana-Poros, Santorini and Nisyros span the ~400 km from the west to the east side of the Aegean arc. The thickness of the continental crust decreases from west to east, and published isotope data indicate that the amount of crustal contamination of the magmas does likewise. This model is supported by the presence of quartz xenocrysts and zircons in the western volcanic centres, and their virtual absence in Santorini-Nisyros.

Other features do not show such regular variation along the arc. Aegina-Methana-Poros, post-caldera Nisyros and the earliest Santorini deposits resemble each other by consisting mainly of lava domes with abundant enclaves, by the almost ubiquitous presence of amphibole and fairly constant FeO*/MgO ratios with increasing silica content of the magmas. This contrasts with the post-300 ka Santorini deposits, which consist of lava flows and abundant pyroclastic deposits, with few mafic enclaves and virtually no amphibole.

Both Nisyros and Aegina have high contents of Sr for a given degree of differentiation (400-1000 ppm for basaltic andesites), whereas Santorini and Methana-Poros samples never exceed 400 ppm Sr. The high contents of Sr in Aegina are not matched by similar enrichments in other fluid-mobile elements, such as Ba or Rb. The post-300 ka Santorini deposits show a clear increase in Y with differentiation, which is not observed in the other volcanic centres; this may reflect the role of amphibole fractionation.

New radiogenic isotope data will be presented to shed more light on the origin of the geochemical, mineralogical and morphological variations between the islands studied.

Volatility of nuclei mode arctic aerosol

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New particle formation should be extensively investigated due to its strong variability, non linear dependence on anthropogenic or natural precursors and the potential effect on climate in a regional and global scale. It has also recently emerged that at certain areas part of newly formed particles is not volatile at temperatures between 250-300°C. At these temperature range particles consisting of sulphuric acid or sulphate should be fully volatile. In order to test the above described hypotheses measurements of the volatility of sub-200-nm ambient particles were conducted in the Arctic background lower troposphere, at the Ny Aalesund Zeppelin GAW site. Nyeki *et al.*, [1] have presented results for the semi volatile and refractory aerosol fractions at Ny Aalesund. A volatility tandem DMA (VTDMA) system was set-up and was operated during a period of three months. Thermal processing at three temperatures 30, 110 and 280°C was achieved by an improved low flow volatility tube [2]. The system monitored the volatility of particles having nominal mobility diameters (i.e., diameters dialled by the first DMA in the system) of 18, 40, 150 and 200 nm in a continuous mode. The thermal behaviour of the nucleation mode particles was examined by selecting particles having 18 nm nominal diameter. At least two occasions of increased nucleation mode particles were detected. The appearance of these particles is characterized by the absence of equivalent increase in the Aitken and accumulation mode particle number concentration. It is observed that particle numbers of the nuclei mode particles plummet at the high temperature. This is an indication that the particles consist of ammonium sulphate or bisulphate.

[1] Nyeki *et al.* (2005) *Tellus B* **57** (1) 40-50. [2] Fierz *et al.* (2007) *J. Aerosol Sci.* **38** (11) 1163-1168

Tracking nitrogen dynamics in the lower Qishon stream system (Israel) using nitrate stable isotopes

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Estuaries are presumed to have a significant role in controlling nutrient fluxes from land to sea, affecting nutrient loads to coastal waters. They may serve as a significant nitrogen sink, owing to biotic removal by assimilation, denitrification or by burial processes, and also as a source of nitrogen via degradation of organic matter.

In this research we investigate the nitrogen sources and biological mediated processes in the semi arid estuary of the Qishon Stream (Israel). This by nitrate stable isotopes measurements ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$) combined with additional chemical analyses of the water column and sediment porewater. The relative importance of the above processes ultimately influence the load of inorganic nitrogen exported to the Mediterranean coastal waters.

The results indicate the dominance of different nitrogen sources at the lower and upper stream system. The upstream station is dominated by sewage derived nitrogen while the downstream stations reflect the mixture of additional local industrial sources.

Seasonal scale measurements indicate significant removal of nitrogen by assimilation in surface waters during spring, summer and fall, and denitrification in the sediments. On the other hand, high sulfate availability via seawater intrusion combined with high organic matter loading in this eutrophic system, support high rates of organic matter remineralization via anaerobic sulfate reduction, generating high flux of ammonium into the water column.

$(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ disequilibria in fresh and altered Kolbeinsey Ridge basalts

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Here we report measurements of U and Th isotopes for 27 young (<10 ka) mid-ocean ridge basalts (MORB) from the slow-spreading Kolbeinsey Ridge north of Iceland (67°05'–70°26'N). The basalts display both $(^{230}\text{Th}/^{238}\text{U}) < 1$ and $(^{230}\text{Th}/^{238}\text{U}) > 1$, with $(^{230}\text{Th}/^{238}\text{U})$ ranging from 0.95 to 1.30. Kolbeinsey Ridge samples lie in a narrow range of $(^{230}\text{Th}/^{232}\text{Th})$ (1.20 – 1.32) with a correspondingly large range in $(^{238}\text{U}/^{232}\text{Th})$ (0.94 to 1.32), producing a horizontal array on a $(^{230}\text{Th}/^{232}\text{Th})$ vs. $(^{238}\text{U}/^{232}\text{Th})$ 'equiline' diagram. Kolbeinsey Ridge Nd, Sr, Hf, and Pb isotopic compositions are relatively depleted and show a limited range (e.g. $\epsilon_{\text{Nd}} = +8.4 - +10.5$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70272 - 0.70301$, $\epsilon_{\text{Hf}} = +15.4 - +19.6$, and $^{208}\text{Pb}/^{206}\text{Pb} = 2.043 - 2.095$). We measured $(^{234}\text{U}/^{238}\text{U}) > 1.005$ in 12 basalts, likely reflecting post-depositional contamination by chemical interaction with seawater. Our measurements further show that samples with low $(^{230}\text{Th}/^{238}\text{U})$ have high $(^{234}\text{U}/^{238}\text{U})$, whereas Kolbeinsey MORB with $(^{234}\text{U}/^{238}\text{U})$ of unity have universally high $(^{230}\text{Th}/^{238}\text{U})$. The correlation between $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ for Kolbeinsey lavas suggests a systematic alteration process affecting both U and Th isotopes in these MORB.

Effects of retrogression on trace element contents of metabasites, Ile de Groix, France

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The metabasites of the Ile de Groix - part of a Hercynian HP/LT metamorphic belt - constitute the remnants of subducted oceanic crust. Trace elements contents in the blueschist GR 25a and the nearby outcropping retrograde greenschist GR 25b (whole rock and minerals) were analysed by LA-ICP-MS [1] to understand the behaviour of trace elements during retrogression.

Analyses and mass balance calculation indicate that at blueschist facies conditions, garnet is the main host for HREE, while epidote contains more than 95 % of Th, U, Pb, Sr and LREE. MREE are also preferentially incorporated into epidote. Ti and Nb are concentrated in rutile and titanite, the latter being also rich in HREE. Cs, Rb and Ba are hosted in phengite. The contribution of amphiboles (glaucofan, barrosite and actinolite) and iron oxides in the trace element mass balance is negligible. During the retrogression, garnet became unstable and was partially altered to chlorite. HREE liberated from garnet alteration were mainly trapped in newly formed titanite, whereas retrograde albite contains Sr and Ba.

The comparison of whole rock compositions between blueschist and retrogressed greenschist shows that the REE and HFSE have been largely immobile, whereas the LILE contents must have changed. REE and HFSE were not able to leave the system during retrogression, since these elements are mainly hosted by epidote and titanite that remain stable under retrograde conditions. The contents of Rb, Ba, K contents and, to a lesser extent, the contents of Th and U, have decreased during the retrogression. This can be interpreted as a result of partial mobilisation of these elements during interaction with the fluid responsible for the rehydration of the rock. The isothermal decompression associated with the rehydration process has led to the breakdown of phengite and crystallisation of a second generation of phengite. During this process, a part of the LILE content was incorporated into newly formed minerals (albite and phengite II), while some amount of the LILE sequestered into the percolating fluid has left the rock.

[1] El Korh *et al.* (2009) *Journal of Petrology*, (submitted).

Slab components in the Mariana arc: Light, heavy and novel

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The isotopic composition of Li promised huge potential as a tracer of slab components in arcs. Altered oceanic crust and most sediments entering the subduction zone are heavy, fractional dehydration processes should only accentuate this signature in fluids released from the slab and arc lavas are elementally enriched in Li. Surprisingly, very few arcs show any indication of a heavy Li isotope signature. We have analysed several arcs in detail and find no evidence for a heavy slab component. Yet this negative result is important as it indicates considerable exchange between slab-derived fluids and the mantle wedge, likely aided by the high diffusivity of Li and the large Li reservoir represented by mantle olivine.

Interaction of slab derived components with the mantle is an important consideration in accounting for the notable U-series disequilibria seen in island arc lavas and the Marianas in particular. A key observation is that the “fluid” component, linked by Pb isotope measurements to the mafic oceanic crust, has extreme (²²⁶Ra-²³⁰Th) and ²³⁸U-²³⁰Th excesses coupled with ²³⁵U-²³¹Pa deficits. This ensemble of features can be modelled as a result of interaction of a slab component with the mantle at low porosities, although the magnitude of the (²²⁶Ra-²³⁰Th) excesses is not readily explained. Alternatively, residual accessory phases present during slab-dehydration may well have a key but currently poorly constrained role in shaping the U-series disequilibria of the “fluid” component. Such a process has been plausibly invoked to control many element budgets and likely plays a major role for the actinides, but currently there is dearth of information on the partitioning of Pa in key phases such as monazite or allanite.

To this already heady cocktail of light stable and heavy, radiogenic isotopes, the future offers novel insights from transition element isotope measurements. Initial data in Mariana lavas show a range in $\delta^{97}\text{Mo}/^{95}\text{Mo}$, with “fluid” rich samples some 0.3‰ heavier than sediment rich counterparts. Since pelagic sediments are typically heavier than Fe/Mn crusts on altered mafic crust, this sense of difference in Mo isotopes is intriguing and may attractively be related to the process of element transport.

A comparison of Cs/K mass ratios in select micas, soils and kaolins from the Southern Appalachian Piedmont and coastal plain

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Concentrations of K and stable Cs were determined for detrital muscovites separated from Cretaceous and Tertiary Georgia kaolin deposits and for the interlaboratory reference materials KGa-2 (Georgia kaolin), Bern-4M (muscovite from gneiss) and SCo-1 (Cody Shale). Values obtained for the geochemical reference material SCo-1 confirm the accuracy of the analytical methods used. The Cs/K mass ratios measured for two muscovite samples separated from the Georgia kaolins, each about 1.3×10^{-5} , are close to the Cs/K ratio of the Bern-4M muscovite but are an order of magnitude less than the Cs/K ratio for the upper continental crust. The Cs/K ratio of KGa-2 is similar to published values for SCo-1 and other shales, which are a little greater than the ratio for the upper continental crust. Cs/K ratios determined elsewhere for five samples of sandy soil from the Savannah River Site (SRS), whose clay fractions consist mostly of kaolinite and hydroxy-interstratified vermiculite (HIV), are larger than the Cs/K ratio for the muscovites separated from Georgia kaolin. Those muscovites are believed to represent generally the muscovite eroded and transported from the Appalachian Piedmont to be incorporated in coastal-plain sediments. The Cs and K in the SRS soils are thought to be mostly in weathered micaceous phases, HIV in particular. That the Cs/K ratios of the soils are higher than that of the muscovite deposited in the parent sandy sediments suggests that stable Cs has been retained preferentially by the weathered micaceous phases during the genesis of the SRS soils. This finding is consistent with the demonstrated high ion-exchange selectivity of weathered mica (illite in particular) for Cs relative to K and is relevant to construct models describing the sorption and transport of anthropogenic and radioactive Cs-137 in the SRS soils.

Metals pollution of the ancient harbor of Tyre (Lebanon)

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Ancient metal pollutions are well documented by records of lead or copper concentrations in ice (e.g. Hong *et al.*, 1996 [1]) or ombrotrophic peat (e.g. Shotyk *et al.*, 1998 [2]). They originated first in the domestication of fire and second in the discovery of mining and metallurgy (Nriagu, 1996 [3]). The study of archeological contamination of soils and sediments allow to extend the prediction of metal contamination at the millennial scale and to evaluate their potential environmental risk. Tyre northern harbor appears as a suitable setting for such a study, as sediments were deposited in a confined, low energy environment, and acted as a receptacle for the waste produced locally by the activities occurring upstream in the city, via particulate transport, during the last two millennia. Several metals and metalloids profiles, obtained by ICP-MS measurements of harbor sediments are presented here, and used to address the question of the behavior of these elements in a confined, coastal environment. The anthropogenic pollution record, obtained after normalisation by non anthropogenic elements associated with metals and metalloids in the sediments (Th and Nd) is coherent with the history of metals during Antiquity, in terms of the differential onset of metals pollution (e.g. early Pb and late Zn), of the alloys used in the city (e.g. tin bronze) and of the timing of pollution. Apart from their archeological implication, these observations suggest that despite disturbances, mostly due to harbor maintenance, the sequence of metals and metalloids inputs is rather well preserved and perturbation by diffusion does not exceed a few cm even for porous sandy material contaminated 2000 years ago. Other sources of metals and metalloids enrichment are distinguished, using normalisations and ESR spectroscopy of manganese. The apparent lack of post-depositional mobility of metals and metalloids in the sequence is striking, and opens questions concerning the speciation of metals and metalloids in such a suboxic marine setting over the last two millennia.

[1] Hong *et al.* (1996) *Sci. Tot. Environ.* **188**, 183-193.

[2] Shotyk *et al.* (1998) *Science* **281**, 1635-1640 [3] Nriagu (1996) *Science* **272**, 223-224.

Neodymium isotopic composition of North Atlantic Fe-Mn oxides

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Neodymium leached from the ferromanganese (Fe-Mn) oxide coatings on lithogenic material is thought to record the Nd isotopic (ϵ_{Nd}) signature of the overlying water mass [1]. North Atlantic Deep Water (NADW) and Antarctic Bottom Water have distinct ϵ_{Nd} values of -13.5 and -8.0, respectively, thus Fe-Mn oxide coatings have been used to reconstruct large-scale Atlantic circulation [1]. The major components to North Atlantic Deep Water, Iceland Scotland Overflow Water, Denmark Straits Overflow Water, and Labrador Sea Water, also have distinct ϵ_{Nd} values (-8.4, -8.2, and -14.5, respectively) [2], which suggests that Fe-Mn oxide coatings from northern North Atlantic sites could be used to examine the variability in NADW components that has been observed using other proxies [3,4]. However, according to our core top study, proximal sources of easily-leached volcanogenic ash add a complication for the use of the leaching method on sediments from the northern North Atlantic. Fe-Mn leachates from core tops close to Iceland, or directly downstream from Iceland, have ϵ_{Nd} values up to +3.1, while Fe-Mn leachates from more distal sites record ϵ_{Nd} values which match modern bottom water. Volcanogenic material does not appear to be transported to the mid-latitude central North Atlantic, making this an ideal location for using ϵ_{Nd} to track changes in NADW.

Preliminary records of Fe-Mn leachate ϵ_{Nd} have been generated from cores CHN82-23PC, in the central North Atlantic, and VM27-17, in the western North Atlantic. These records suggest that the ϵ_{Nd} value of NADW may have varied on orbital time-scales, possibly due to variations in the relative fluxes of NADW components, or due to changes in continentally derived inputs.

[1] Piotrowski *et al.* (2005) *Science* **307**, 1933-1938. [2] Lacan & Jeandel (2005) *Geochem., Geophys., Geosys.* **6** (12) 1-20. [3] Duplessy *et al.* (1988) *Paleoceanography* **3** (3) 343-360. [4] Hillaire-Marcel *et al.* (2001) *Nature* **410**, 1073-1077.

Stochastic approach to assess a nitrate process-factor in soil water

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In this research, a nitrate process-factor was driven for the Wijlegem catchment, Belgium. The simulated concentration of the water draining from the soil profile (at a depth of 90 cm), instead of the NO_3^- -N concentration in the drainage water, was used to calculate Cg. The NO_3^- -N concentration at the outlet of the catchment was used as Cs. The model was run in a stochastic way on each individual field within the catchment for four consecutive winter periods. A Monte Carlo approach was used (i.e. the simulations are repeated 1500 times with new picks). The process-factor (the ratio of the simulated NO_3^- -N concentration in the soil water at 90 cm and the measured NO_3^- -N concentration in the surface water) for the catchment of the Wijlegem was calculated to be 2.35. The NO_3^- -N concentration in the soil water was simulated with the Burns α model.

The research concluded that, the average process-factor for the four leaching periods is 2.35. This implies that the average simulated NO_3^- -N concentration in the soil water at 90 cm under the field surface is twice the average measured NO_3^- -N concentration in the surface water, or that 50% of the NO_3^- -N will be denitrified in the subsoil. It is thus recommended that, the modelling combined with monitoring in small agricultural catchments is a useful tool for assessing state, trends and effects of counter-measures for water quality management planning aimed at reducing the impact of nitrogen leaching on the aquatic environment.

Impact of mineralogy on groundwater chemistry along the southeastern part of the UAE

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Quaternary clastics sequences represent an important aquifer system in the southeastern part of United Arab Emirates (UAE). During last decade, extensive utilization of groundwater has caused deterioration of the water. Therefore, understanding the water-rock interaction in this aquifer seems indispensable for future sustainable management. In order to achieve this goal, petrological characterization of the aquifer sediments and chemical analyses of the groundwater were carried out. The results indicate that within the determined four facies, serpentine and calcite are the dominant minerals followed by dolomite and plagioclase. Results of the groundwater analyses show relative increase of the Ca^{+2} concentrations within the calcilithite and lithic carbonate facies whereas an opposite trend was observed for the elevated Mg^{+2} concentrations. The latter feature may relate to accompanied effect of serpentinization of olivine in the ophiolite zone recharge area and *in situ* dolomitization of serpentine. The high calcium concentrations reflect disequilibrium in the water system that has been brought about by less recent amount of recharge water to the aquifers. A feature that supports this conclusion is occurrence of extensive calcite coating on ophiolite clasts at zones reflecting fluctuation in the water table.

Minimizing influences of adsorption/desorption processes of analytical systems on isotope ratio measurements

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Measurements of carbon and oxygen isotopes of CO₂ by continuous flow IRMS (isotopes ratio mass spectrometry) is widely used in environmental studies and climate change research, e.g. we are measuring $\delta^{13}\text{C}$ on CO₂ in air from the Dome C ice core. Yet there are problems associated with the reproducibility, in particular for small sample sizes. Namely, potential fractionations in the open-split and difficulties in understanding the non-linearity effect are affecting the results. A method is presented how these fractionations in the open-split can be eliminated. The non-linearity effect is explained by adsorption/desorption processes in the ionisation chamber or its vicinity and is independent on the open-split settings and on the ion source settings. It is just dependent on the amount of CO₂ entering the ion source. The non-linearity can be eliminated by a small additional flux of a specific conditioning gas. For the adsorption process in the mass spectrometer we found a fractionation factor of 0.982 ± 0.005 for $\delta^{13}\text{C}$ and 1.002 ± 0.004 for $\delta^{18}\text{O}$, respectively.

Tracing transformation of organic groundwater contaminants by stable isotope fractionation

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Isotope methods are indispensable for sustainable use of groundwater. Traditional analysis of ²H, ¹⁸O and ³H in water serves to assess groundwater infiltration. The advent of gas chromatography – isotope ratio mass spectrometry (GC-IRMS) has made it possible to trace origin and degradation of single organic groundwater contaminants at low concentrations. A recent US-EPA guide details how isotope ratios of the contaminants may serve as fingerprints to allocate different sources, and how increasingly positive isotope values downstream of a contamination source can show how much of the contaminant has been degraded [1].

Enrichment of heavy isotopes (¹³O, ²H, ¹⁵N) in the remaining compound depends on underlying characteristic kinetic isotope effects during (bio)chemical transformations. My work has shown how such enrichment trends may be used to identify also degradation pathways and mechanisms by which a contaminant is transformed [2]. In particular, if changes in isotope ratios are measured for more than one element and drawn in a dual isotope plot, characteristic trends can make different transformation pathways visible [3, 4].

While past studies have focussed on point source pollutants, future challenges lie in addressing also diffuse contaminants like pesticides. For these new compounds, precise and accurate GC-IRMS methods need to be established [5]. Also, natural concentrations are lower so that non-fractionating enrichment and purification methods are warranted. Finally, source-related isotope patterns need to be distinguished from degradation-related trends. To this end, information from one isotope is generally not sufficient. For isoproturon we show that multi-element (¹³C, ¹⁵N) as well as intramolecular isotope analysis of different molecular fragments provides enhanced information that enables a detailed mechanistic study of transformation reactions [6].

[1] Hunkeler *et al.* (2008) *EPA 600/R-08/148*. [2] Elsner *et al.* (2005) *Environ. Sci. Technol.* **39**, 6896-6916. [3] Zwank *et al.* (2005) *Environ. Sci. Technol.* **39**, 1018-1029. [4] Elsner *et al.* (2007) *Environ. Sci. Technol.* **41**, 5693-5700. [5] Meyer *et al.* (2008) *Environ. Sci. Technol.* **42**, 7757-7763. [6] Penning *et al.* (2008) *Environ. Sci. Technol.* **42**, 7764-7771.

Fluid inclusion of Pan-African high grade metamorphism of Southern Sinai, Egypt

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Fluid inclusions in the leucosomes of Wadi Feiran migmatites show that CO₂, H₂O and (H₂O-CO₂) fluids were likely to have been present when partial melting began in these rocks. Low salinity, aqueous fluid, to lesser extent CO₂ rich, fluids are the most abundant fluids. The present study suggests that high density CO₂ inclusions were formed at the earliest stage, while H₂O inclusions were formed at a later stage. In an intermediate stage, low density CO₂ and H₂O CO₂ inclusions were formed. At the early stage of uplift and during the melt crystallization, the CO₂ bearing vapors were trapped at grain boundaries. At the late stage of uplift, H₂O released at the time of crystallization of the melt was trapped as inclusions.

Origin of pargasitic megacryst in the neogene volcanic rocks of central Iran

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The exposure of Neogene volcanic rocks mainly in Qom province in Iran that belongs to the Urumieh-Dokhtar Magmatic Arc (UDMA) as Sakht-e-Hesar and Khastak area (Fig. 1). The Neogene volcanic activities are divided into two phases: Ngv₁ and Ngv₂. At the first stage (Ngv₁), volcanic rocks contain basalt to andesitic-basalt as lava or pyroclastic materials. The explosive event was followed by the volcanic to sub-volcanic associations of Ngv₂ with products of mainly andesitic to rhyolitic composition (second stage) [1]. This volcanic complex consists of few centimetre amphibole megacrysts that mineral geochemistry analyses present them as pargasite. These amphiboles transformed to pyroxene, plagioclase and magnetite which indicate reaction between sub-alkaline magma and pargasite megacrysts. It seems that these megacrysts are originated from metasomatized mantle during fractional melting. Probably, these amphiboles ascend and emplacement in magma chamber and non-equilibrium geochemistry relation was found with saturated melt. The mantle metasomatism patterns in this area are inferred from subduction of the Neo-Tethys beneath mantle wedge of the Central Iranian Block during Mesozoic period.

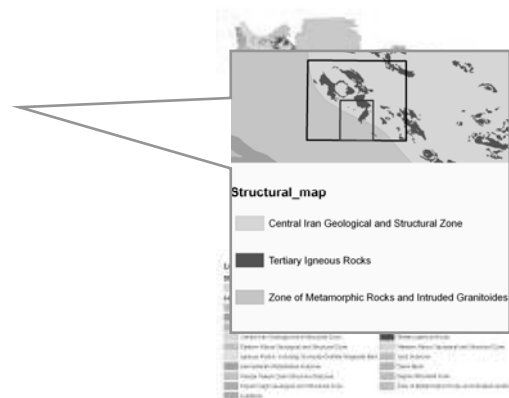


Figure 1: Structural map of Iran and selected Neogene complex

[1] Emami (1991) Explanatory text of the Qom quadrangle map, Geological Quadrangle No. E6, Geological Survey of Iran.

Stimulation of natural organohalogen formation by microorganisms

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Halogenated C1 and C2 hydrocarbons contribute to a significant extent to atmospheric ozone destruction. They are emitted among other sources from salt lake sediments [1]. Organohalogens are formed biotically by the catalytic activity of plants, animals and microorganism. Organohalogens can form also abiotically in presence of humic compounds, KCl and Fe(III) minerals. The abiotic formation is greatly enhanced by addition of H₂O₂ suggesting the involvement of radicals [2]. When microorganisms reduce humic substances electrons can be shuttled to Fe(III) minerals and semiquinone radicals are formed [3]. This suggests that organohalogen formation in natural environments could also be stimulated indirectly through the activity of microorganism catalysing Fe- and humic substance-redox transformations. We performed batch experiments with Fe-metabolizing bacteria, Fe minerals and humic compounds and quantified organohalogen formation by GC-MS. In addition, we characterized the microbial communities in sediment samples from South African salt lakes using both cultivation-dependent (MPN counts) and cultivation-independent (DGGE) methods. The aim of this study is to determine how and which microorganisms affect organohalogen formation indirectly through iron or humic substance redox transformations.

- [1] Weissfolg *et al.* (2005) *Geophys. Res. Letters* **32**.
[2] Keppler *et al.* (2006) *ES&T* **40**, 130-134.[3] Lovely *et al.* (1996) *Nature* **382**, 445-448

Characterisation of organic compounds in atmospheric aerosols utilising a GCxGC/MS-TOF

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Aerosols consists of various inorganic and organic chemical species, of which only a small fraction of organic compounds have been identified. Current methods give valuable information with regards to the overall chemical composition, oxidation state and reactivity of organic aerosols, but they provide limited information about the actual character of individual organic compounds [1]. Two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer (GCxGC/MS-TOF) is a relatively novel technique that has the potential to measure and characterise organic compounds within complex matrices, such as ambient particulate matter [2]. The main aim of this investigation was therefore to collect and extract organic particulate matter, followed by analyses of the samples with a GCxGC/MS-TOF in order to identify new organic compounds in ambient air.

Samples were collected at Elandsfontein in the Mpumalanga province of South Africa. Elandsfontein is an air quality monitoring station situated between coal-fired power stations in the Mpumalanga Highveld. A high-volume air sampler equipped with a quartz filter and polyurethane filter (PUF) was used.

Two different extraction methods namely: soxhlet extraction and accelerated solvent extraction (ASE) was compared. Different combinations of solvents were used with each of the two different extraction methods in order to extract polar and non-polar organic compounds.

A state-of-the-art LECO Pegasus 4D GCXGC/TOF-MS that was recently procured by the university was used for analyses. Compounds were characterized according to their confirmation- and quantification ions.

- [1] U. Poschl (2005) *Angew. Chem. Int. Ed.* **44**, 7520-7540.
[2] Welthagen *et al.* (2003) *J. Chromat. A* 1019, 233-249.

Diel patterns and deposition of atmospheric Hg species at nine inland and coastal sites

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To examine cycling and deposition of atmospheric mercury (Hg), we conducted several field studies across the central and eastern United States over the last 5 years. As part of this study, concentrations of atmospheric Hg species were measured at nine inland and coastal sites (36-364 days of data per site) including heavily industrialized inland areas (East St. Louis, IL and Milwaukee, WI), remote inland locations (Lostwood, ND; Devil's Lake, WI; and Big Meadows, VA), and coastal regions (Weeks Bay, AL; Cape Romain, SC; Woods Hole, MA; El Yunque, Puerto Rico).

Seasonal elemental Hg concentrations at these nine sites ranged from 1.27±0.31 to 2.94±1.57 ng m⁻³ and were greatest during the spring and winter and at sites near large local Hg sources. Seasonal reactive gaseous mercury (RGM) concentrations ranged from 1.5±1.6 to 63.2±528 pg m⁻³; the season exhibiting the highest RGM differs among sites. The highest RGM concentrations (up to 38,300 pg m⁻³) are associated with heavily industrialized sites (East St. Louis and Milwaukee) impacted by Hg sources such as coal-fired power plants, metal production facilities, and chlor alkali producers. Strong diel patterns with early afternoon maximum RGM concentrations were observed at the three coastal sites impacted by anthropogenic emission sources (Weeks Bay, AL; Cape Romain, SC; Woods Hole, MA) and are indicative of photochemical RGM production.

Total Hg deposition for the sites was determined by summing dry deposition (modeled) of reactive and particulate Hg with wet deposition (measured). Total annual Hg deposition ranged from 5.1 to 66 µg m⁻², with <35% being dry deposition at all sites except for East St. Louis (66%). Regional Hg emission and calculated deposition are weakly correlated. These findings suggest that further work is required to determine if there is a relationship between regional emission sources and Hg deposition.

Aerosol characteristics in rural and remote areas of south China

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Introduction

The Asian continent and China in particular is an important source region of aerosol particles, while the understanding regarding the aerosol chemical characteristics and sources is limited. Therefore, an intensive field campaign was conducted in south China to investigate the major chemical components of the ambient aerosol and to estimate source contributions, using molecular markers.

Experimental

Sampling was conducted at eight stations across south China, including urban, rural and remote sites, such as Hong Kong, Hainan Island and Tengchong. Aerosol samples were collected in two size ranges (PM_{2.5} and P₁₀), using Mini-vol air samplers, with a typical sampling frequency of 24 hours.

Samples were analyzed for organic carbon (OC) and elemental carbon (EC), using a thermo-optical transmittance (TOT) protocol. Molecular tracers for biomass burning, fungi tracers and other polar organic species were measured by high-performance anion exchange chromatography (HPAEC).

Results

Various types of sources, including biomass burning and primary biogenic processes, influenced the aerosol composition in south China during the time frame of this study. The Pearl River Delta (PRD) region showed a particularly complex source signature, including local as well as long-range transport impact.

Biomass burning smoke had significant contributions to ambient aerosol at some of the sites, such as Tengchong, a remote site in the south-eastern part of the Tibetan Plateau, influenced by agricultural fires in south and south-east Asia.

Biogenic aerosol contributions were determined on the example of fungi tracers (i.e., arabitol and mannitol, with ambient concentrations of more than 100 ng m⁻³ each), showing important contributions of microbial activity, specifically at subtropical locations, such as Hainan Island.

Temporal isotopic variations of dissolved silicon in a pristine boreal river

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Interest in quantifying the biogenic impact on the terrestrial biogeochemical Si cycle has increased significantly since biological control has been suggested. Previous observations of isotopic fractionation of Si during biogeochemical and geochemical processes imply that seasonal dissolved Si isotopic patterns in rivers have the potential for use in extracting information about the riverine- and terrestrial biogeochemical Si cycles.

Therefore, variations in the isotopic composition of dissolved riverine Si were investigated for the Kalix River, Northern Sweden, one of the largest pristine rivers in Europe, based on high-frequency sampling during a period of 25 weeks from early April to early October 2006. Temporal variations spanning 0.4‰ for $\delta^{29}\text{Si}$ and 0.8‰ for $\delta^{30}\text{Si}$ of dissolved Si in the Kalix River were observed during the period, suggesting that the riverine Si input to the oceans cannot be considered to have a constant Si isotopic composition even on a short time scale.

The results implicate biogeochemical Si-cycling via formation and dissolution of biogenic silica as major processes controlling the Si transport in boreal systems. The Si budget in the river system appeared to be controlled by relative Si accretions during high discharge events and relative Si depletions in the subarctic mountainous and lake dominated areas. There were also temporal variations in Si isotopic composition with accretion (relative Si contribution), accompanied by depletion of the heavier Si isotopes, while the opposite trend was observed during periods of riverine Si depletion. These isotope variations can be explained by release of plant derived silica, depleted in heavier Si isotopes, during the spring snowmelt. Further, increased volumetric contribution from the headwater and losses of Si due to biogenic silica formation by diatoms in the subarctic lakes at a later period are expected to be responsible for the preferential losses of lighter isotopes. These conclusions are further verified by land cover analysis.

Metasomatic crystallisation of sapphirine during Mg-enrichment of gabbros

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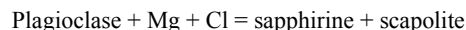
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Metasomatism in the Bamble Sector, South Norway, caused scapolitisation and albitisation on a regional scale. Scapolitisation is associated with veining, and transformed metagabbros pervasively over areas of up to 1-2 km². The contact between pristine gabbro and scapolitised metagabbro is sharp and observed over distances of only a few mm. The boundary is interpreted to represent a fluid front progressing as an initial hydration (amphibolitisation) followed by Cl-saturation and K-saturation, transforming the gabbro to metagabbro dominated by scapolite (Me₁₉₋₄₂), edenite and rutile. Presence of sapphirine, enstatite, and a high content of phlogopite and chlorapatite correlate with intense scapolitisation in the vicinity to the fluid channels. Studies on the mineral replacement reactions and the mineral chemical evolution constrain the composition of the scapolitising fluid to be a hydrous volatile rich in Cl, P, and K, enhancing enrichment in Mg and depletion of Fe.

The sapphirine ((Mg_{3.4}Fe_{0.1}Al_{4.5})(Al_{4.5}Si_{1.5})O₂₀) occur as tiny needles (< 0.02 mm) in scapolite. Its crystallisation is observed related to the replacement of plagioclase ((Na_{0.5}Ca_{0.5})(Al_{1.5}Si_{2.5})O₈) to scapolite (Na₃Ca₁Al_{3.8}Si_{8.2}O₂₄(Cl_{0.9}(CO₃)_{0.1})), consuming the excess Al released during the mineral reaction. The reaction can in a simplified form be written:



The scapolitisation cause a typical Mg-enrichment of the rock, stabilizing the Mg-rich end member of the mafic phases phlogopite (#Mg=0.95), amphiboles (#Mg=0.81-0.87) and enstatite (#Mg=0.95-0.96). The occurrence of sapphirine during scapolitisation show that the Al-Mg-phase can form in gabbro during strong Mg-metasomatism. Mg-rich rocks as cordierite-anthophyllite-schists occur along the margins of the metagabbros, and are interpreted as result of Mg-enrichment of gabbro during metasomatism.

Speciation and isotopic signatures of Hg in the Lake Baikal – Angara River food-web

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Toxicity of Hg is well known. Once Hg(II) enters the ecosystem, it is converted to the toxic MeHg by bacteria, then accumulates throughout the aquatic food-chain. Fish tend to concentrate mercury by a factor of 10^5 - 10^7 compared to Hg water content, which can lead to dangerous levels in fish even in areas with tolerable aquatic Hg(II) concentration.

In this work we investigated Hg signatures in the Lake Baikal ecosystem. Different trophic levels were studied: plankton, herbivorous fish – roach (*Rutilus rutilus lacustris*) and carnivorous fish – perch (*Perca fluviatilis*). Different size and age fish-species were obtained from Lake Baikal (LB) and from Angara River (AR). LB samples were collected in a pristine area, while AR samples were collected in the anthropogenically Hg-contaminated Bratsk water-reservoir. The main source of anthropogenic Hg (Hg electrolysis plant) was closed in 1998.

Summary of the results are presented in the Table below. Total Hg concentration is presented for freeze-dried samples. Samples of the lower level in the food-chain shows lower concentrations of the total Hg. Same species from Hg-contaminated region (Bratsk) have 5-11 times higher concentration of Hg. The relative content of MeHg (%) in AR samples was found to be slightly lower. Isotopic composition of Hg was measured using Nu PlasmaHR. Mass-dependent (for ²⁰⁴Hg, ²⁰²Hg, ²⁰⁰Hg, ¹⁹⁸Hg) and mass-independent (for ²⁰¹Hg, ¹⁹⁹Hg) fractionation is observed. This fractionation proves that the magnetic-isotope effect plays an important role in the environmental reactivity.

Food-web sample	total Hg, $\mu\text{g kg}^{-1}$	MeHg, %
Plankton (LB)	25 ± 7	12.4
Roach (LB)	204 – 479	91.6 – 97.9
Perch (LB)	427 – 1214	89.9 – 97.3
Plankton (AR)	55 ± 11	51.5
Roach (AR)	1034 – 5209	89.4 – 94.4
Perch (AR)	3197 – 11676	88.8 – 95.3

Table 1: Summary for total Hg and MeHg concentration in Lake Baikal – Angara River food-web samples.

The response of Cretaceous calcareous nannoplankton to $p\text{CO}_2$ and ocean acidification

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Recent environmental change and instability pose urgent questions regarding biota ability to keep pace with excess CO_2 , increase in acidity and drop in pH of surface waters. Calcareous nannoplankton cannot efficiently calcify if the medium acidity passes a critical level, but laboratory studies are not conclusive as to assess crises, adaptations, evolutionary innovation and/or extinctions. The geological record indicates that ocean biota can adapt to higher acidity, but while the current decrease in pH is compressed in a very short period of time, past changes in oceanic acidity occurred over tens of thousands of years, giving time for life to adjust or even take advantage.

Within the oceanic biosphere, calcareous nannoplankton play a key-role as is abundant from coastal to open ocean settings, has a 220 My-long evolutionary history, is one of the most effective calcite producers of the planet, and is extremely sensitive to environmental variations. We explored cases of excess CO_2 derived from major volcanic episodes and marked by calcareous nannoplankton changes in evolutionary rates, species richness, abundance, and calcite production.

Available stratigraphy and cyclochronology allow high-resolution dating of biotic and environmental fluctuations, providing the precision necessary for understanding the role of $p\text{CO}_2$ and ocean acidification on nannoplankton biocalcification and evolution. Selected case histories are the Aptian and the latest Cenomanian, corresponding to the onset and climax of the mid-Cretaceous SuperGreenhouse, respectively. During formation of the Ontong Java-Maniniki and Caribbean Plateaus, rapidly increasing $p\text{CO}_2$ reached values as high as 2000 ppm, causing a calcification crisis and accelerated evolutionary rates. Maximum ocean acidification, was preceded by a 0.5-1 my-long period of biocalcification decline, dwarfism and production of “deformed-malformed” coccoliths. During the Aptian, the acidification climax lasted some 200 ky and is marked by short-lived abundance peaks of peculiar nannoliths, perhaps representing alkalinity recovery following CaCO_3 dissolution.

As far as evolution is concerned, rising $p\text{CO}_2$ triggered false extinctions (Lazarus effect) among calcareous nannoplankton; conversely, a major origination episode perhaps represents a biocalcification strategy to overcome ocean acidification.

Accumulation of arsenic in polluted and unpolluted small watersheds in Central Europe

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To assess the fate of anthropogenic arsenic in ecosystems, we constructed arsenic input/output mass balances for three polluted and one relatively unpolluted forest watersheds in the Czech Republic. The sites spanned a 6-fold arsenic pollution gradient, and hydrochemistry was monitored for 11 water years (1995-2006). Two of the four sites currently exhibit large net arsenic export via runoff solutes ($5 \text{ g As ha}^{-1} \text{ yr}^{-1}$). This contrasts with previous studies which concluded that upland forest catchments are a net sink for atmospheric As both at a time of increasing and decreasing pollution. The amount of exported arsenic closely correlated with water fluxes via runoff.

Six replicate samples of the following organic-rich materials were taken in spruce stands in 2003-2004: spruce needles class 1, spruce needles class 2, moss *Pleurozium schreiberi*, grasses *Calamagrostis villosa* and *Deschampsia flexuosa*, soil horizons O₁, O_F, O_h, Ah, and B. Thirty samples of fresh bedrock were also obtained from outcrops in each catchment and pooled for As analysis. Spruce tree rings were sampled from one tree per site by sampling full ring-shaped wood segments, each spanning 5 years. Atmospheric deposition of As at individual sites decreased in the order JEZ \geq UDL $>$ UHL \gg LIZ. Arsenic concentrations were significantly higher at JEZ than at LIZ in seven out of eight types of solid samples of ecosystem compartments. In spruce needles, moss, grasses, O and A soil horizons, the most polluted site JEZ had high As concentrations, while the least polluted site LIZ had low As concentrations. The only exception was spruce biomass whose As concentrations (mass-weighted across tree rings) were statistically indistinguishable between JEZ and LIZ. For *Pleurozium schreiberi*, there was a significant positive correlation between present-day atmospheric deposition of As and As concentration in the moss ($R=0.88$). Arsenic concentrations in humus were 400 times higher than in spruce needles. Export of As from catchments via stream discharge was not correlated with the total As soil pool size, which was over 78% geogenic in origin.

Kazdag Massif (NW Turkey): Metamorphic equivalent of the Mesozoic platform of Sakarya continent

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Kazdag Massif (NW Anatolia) has been interpreted as a Paleozoic basement of the Sakarya Continent in the literature [1, 2]. Our recent mapping however has showed that there is an oceanic crust represented by ophiolites as a basement and a platform succession on the top. The platform succession consists in ascending stratigraphic order of a basal conglomerates, thick marbles and metadetrinitic rocks with mafic lava lenses. The basement and the platform succession were metamorphosed under high grade conditions and partly converted into migmatites and metagranites. From the metagranites, ages of $28.2 \pm 4.1 \text{ Ma}$, $26.0 \pm 5.6 \text{ Ma}$ were determined on zircons indicating the age of the metamorphism. The metadetrinitic rocks and migmatites on the other hand had yielded scattered ages from $421.9 \pm 4.1 \text{ Ma}$ to $169.3 \pm 3.5 \text{ Ma}$.

After the metamorphism the Kazdag Metamorphic sequence was internally imbricated and later tectonically overlain by nappes of Karakaya Complex and Çetmi Melange. These nap packages were cross-cut by young granites (18-21 Ma).

The metamorphic platform-type sequence of the Kazdag Massif resembles the non-metamorphic Mesozoic units of the Sakarya Continent. The ophiolitic basement beneath the platform is probably a part of Paleotethys Ocean. The southern margin of the Sakarya Continent was included in the tectonic imbrication during the collision between Tauride-Anatolide Block and the Sakarya Continent, and a slice of this imbrication was metamorphosed to form the Kazdag Massif.

[1] Okay *et al.* (1996) *Tectonics of Asia*, Cambridge U. Press, pp. 420-441. [2] Okay & Satir (2000) *Geol. Mag.* **137**, 495-516.

Formation of water-bearing 2D-defects: An intended case study on xenoliths from the Letseng mine

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Mantle convection and resulting plate tectonics on Earth are strongly influenced by water exchange between mantle and surface. The water in Earth's mantle was thought to reside and move only through point defects in nominally anhydrous minerals (NAMS) such as olivine, pyroxene and garnet. Recent studies by Sommer *et al.* [1] show that water in NAMS is also located in microscale halos around nanoscale 2D-defects like grain boundaries and cracks. They suggest that a considerable amount of mantle-water is stored around these defects. Grain boundaries and cracks in NAMS would therefore play a crucial role for the dynamic planetary water cycle and associated processes in Earth's mantle. Samples for the study will be collected from the Letseng Diamond Mine in northern Lesotho. The mine comprises two economic interesting pipes which consist of Group 1 kimberlite. The pipes have been emplaced in the Cretaceous (~90 Ma), penetrating Jurassic Drakensberg basalts in the vicinity of the southern border of the Kaapvaal Craton [2, 3]. The kimberlites contain numerous mantle and lower crustal xenoliths, including for example garnet-bearing gneisses and granulites, granular lherzolites and harzburgites, as well as megacrysts of olivine and garnet [3]. Samples from Letseng are therefore ideal for case studies on water-bearing grain boundaries and cracks in NAMS of Earth's mantle. Aim of the study is to demonstrate that a considerable amount of mantle-water is embedded around 2D-defects in NAMS. Objectives are therefore to point out the formation of cracks and grain-boundaries as well as the volatile transfer and the physico-chemical properties in and around those defects. Thus, a series of measurements using FT-IR and Nano Sims must be undertaken on samples from mantle xenoliths. To visualise the results we plan to provide 2D-plots and 3D-models of cracks and grain boundaries.

[1] Sommer *et al.* (2008) *Miner Petrol* **94**, 1-8. [2] Field *et al.* (2008) *Ore Geology Reviews* **34**, 33-75. [3] Hopp *et al.* (2008) *Lithos* **106**, 351-364.

Late Mesozoic subduction-induced gold metallogensis along the eastern Asian and northern Californian margins: Efficacy of oceanic versus continental lithospheric underflow

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During latest Jurassic-Cretaceous subduction of paleo-Pacific lithospheric plates, numerous gold deposits formed in the Dabie-Sulu belt of east-central China + its east-Asian extensions, and in the Klamath Mountains + Sierra Nevada Foothills of northern California. Earlier stages of transpression and continental collision at ~305-210 Ma generated a high pressure-ultrahigh pressure (HP-UHP) orogen in eastern Asia, but failed to produce widespread felsic magmatism or abundant gold deposits. Similarly, mainly transform slip involving minor transtension-transpression resulted in the stranding of oceanic terranes in northern California over the interval ~380-160 Ma, but produced only modest granitoid magmas and few important concentrations of gold. In both continental margin realms, nearly orthogonal Cretaceous subduction of oceanic-crust-capped lithosphere resulted in sustained underflow that, reaching magmagenic depths, gave rise to subduction-zone fluids and voluminous intermediate and felsic arc magmas. Ascent of these plutons into the brittle upper crust released CO₂ ± S-bearing aqueous fluids and/or devolatilized the adjacent heated, contact-metamorphosed wall rocks. Hydrothermal fluids transported Au to geochemical sites of abruptly contrasting composition (e.g., serpentinites), precipitating the gold. In marked contrast, where sialic crust was subducted to magmagenic depths, only minor production of granitoid melts occurred (e.g., Late Paleozoic Appalachians, Permo-Triassic east-central China, and Cenozoic Himalayas + Alps), and few coeval ore deposits formed. Mobilization of precious metal-bearing fluids in arc environments apparently requires the long-continued descent of oceanic lithosphere.

Ultra high-pressure tourmalines

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The temperature and pressure stability of tourmaline is very large. It ranges from diagenetic/epigenetic to high-grade metamorphic and magmatic conditions. In this investigation tourmalines from metamorphic rocks occurring in three ultra high-pressure (UHP) localities were structurally and chemically characterized in order to generate accurate structural formulae and to test for any systematic response related to varying temperatures and pressures. Dravite from the Parigi, Dora Maira, Western Alps, Italy locality (~3.7 GPa, 800°C) has the formula $X_{0.9}Na_{0.1}Ca_{0.1}Y_{1.8}Mg_{1.0}Al_{1.0}Fe^{2+}_{0.1}\square_{0.1}Z_{1.5}Al_{5.1}Mg_{0.9}(BO_3)_3T_6Si_6O_{18}V_3(OH)_3W_3[(OH)_{0.7}F_{0.3}]$, with cell dimensions of $a = 15.935(1)$, $c = 7.201(1)$ Å. Dravite from the Lago di Cignana, Western Alps, Italy locality (~2.7-2.9 GPa, 600-630°C) has a formula of $X_{0.8}Na_{0.2}Ca_{0.1}\square_{0.1}Y_{1.6}Mg_{1.6}Al_{0.8}Fe^{2+}_{0.5}Mn^{2+}_{0.1}Z_{1.5}Al_5Mg(BO_3)_3T_6Si_6O_{18}V_3(OH)_3W_3[(OH)_{0.7}F_{0.4}]$ with cell dimensions of $a = 15.945(1)$, $c = 7.210(1)$ Å. "Oxy-schorl" from the Saxony Ore Mountains, Germany locality (>2.9 GPa, 870°C) has the formula $X_{0.9}\square_{0.1}Y_{1.6}Al_{1.6}Fe^{2+}_{1.2}Ti^{4+}_{0.1}Z_{1.5}Al_5Mg(BO_3)_3T_6Si_6O_{18}V_3(OH)_3W_3[O_{0.8}F_{0.1}(OH)_{0.1}]$ with cell dimensions of $a = 15.929(1)$, $c = 7.183(1)$ Å. There is no structural evidence for significant substitution of Si by Al or B in the UHP tourmalines (<T-O> distances ~1.620 Å), even in tourmaline from the highest temperature sample from the Saxony Ore Mountains. This contrasts with tourmalines formed at high grade, but lower pressure conditions having significant amounts of ^{41}Al . For this limited data set there is a very good positive correlation between the sum of ^{61}Al in the UHP tourmalines and the determined temperature conditions of tourmaline formation of the different localities. Furthermore there is a highly negative correlation between the <Y-O> distances of the UHP tourmalines and the temperature conditions of tourmaline formation. Hence, an Al-Mg disorder between the Y and the Z site seems to be dependent on the temperature during crystallization. Because of the very limited localities with the occurrence of UHP tourmalines more extensive detailed studies are not currently possible. Consequently, to further elucidate the relations between metamorphic conditions and the crystal chemistry of tourmalines, efforts will be concentrated on diagenetic to high-grade metamorphic tourmalines from petrologic well characterized environments.

Development of a hyphenated technique (HG-ICP-MS/HG-MC-ICP-MS) for isotopic study of germanium species

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Germanium (Ge) is a trace metalloid which has a strong chemical similarity to silicon (Si). In the oceans, inorganic Germanium (Ge_i) exhibits nutrient-like properties and is closely correlated with silica concentrations in the water column. Germanium is one of the rare elements which presents organic forms (Methyl and Dimethyl) characterized as unreactive in natural environment. Their behaviours have been deduced by their constant concentration over the water column and into the different oceans. But their sources, sinks and interaction with Ge_i cycle remain unknown.

In previous studies, Rouxel *et al.* [2] and Siebert *et al.* [3] developed a new technique of hydride generation to introduce Ge into the MC-ICP-MS. Rouxel and collaborators [4, 5] preconcentrate the inorganic germanium in aqueous samples by Mg precipitates and then analyzed by hydride generation.

In our study, we adapted the method of online hydride generation coupled to a MC-ICP-MS [2, 3] to measure of mono-elemental specie standards (MMGe and DMGe Alfa Aesar JMC). We have studied and optimized the operational conditions to volatilize the germanium species and assess any related fractionation. An online hydride gas injection (Cetac, HGX-200) of the different species is bracketed by traditional spray chamber introduction to measure the hydride volatilisation effects of reaction time, pH of the reaction (acidity of the sample, concentration of the reagent), matrix effects (addition of Iron, L-cysteine) on the precision and accuracy of the isotope ratio. This work on individual fractionation of germanium species will be later followed by an online hyphenated system on natural samples.

- [1] Froelich & Andrea (1981) *Science* **213**, 205-207.
[2] Rouxel *et al.* (2006) *GCA* **70** (13) 3387-3400. [3] Siebert *et al.* (2006) *GCA* **70** (15) 3986-3995. [4] Escoube *et al.* (2008) *EGU2008-A-12035*. [5] Rouxel *et al.* (2008) *GCA* **72** (12) A809

Availability of nutrient sources for bacterial development in deep clay environments

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It is now acknowledged that highly adapted bacteria are present in deep environments and will probably play a very important role in geochemical cycles. The availability of nutrients and energetic sources able to be used by deep biosphere is a key point to understand microbial subsurface life. However the introduction of nuclear waste in a deep geological disposal will lead to a new inventory of nutrients and energetic sources for microbial activity in this particular environment [1]). An inventory of nutrients, energetic sources and possible thermodynamically reactions has been realised in the case of the specific french geological disposal of nuclear waste based on a multibarrier system involving a host rock: argillite. Different reservoirs of nutrients have been identified to be able to support bacterial activity. That is to say: minerals of the host rock, organic matter of the host rock, nutrients of the interstitial water of argillite and hydrogen. H₂ is known as one of the most energetic substrates for deep terrestrial subsurface environments [2]. High amount of H₂ gas will be produced within nuclear deep waste repository (originated from radiolysis or corrosion processes of metallic components in anoxic conditions) and consequently will improved microbial activity in this specific environment. It is known that bacteria developed processes such as complexation, acidification or oxydo-reduction reactions, to access to nutrients contained in minerals [3].

In such a context, we considered in a first step the biological redox reactions using H₂ and Fe (III), and we try to answer the question: are hydrogenotrophic microorganisms able to use structural Fe (III) of the clayey host-rock as electron acceptor?

Kinetic studies of redox metabolism of the iron-reducing bacteria '*Shewanella putrefaciens* strain MR-1' using H₂ as electron donor show availability of Fe (III) as electron acceptor in the studied clayey environment. The use of cristallochemistry tools allow to observe a structural modification of argillite due to this bacterial activity.

The bioavailability of other nutrients in the host-rock will be also discussed in the presentation

IRSN contribution to this work is gratefully acknowledged.

[1] Lin *et al.* (2005) *Geochimica et Cosmochimica Acta* **69**, 893-903. [2] Stroes-Gascoyne *et al.* (1998) *Environmental Science & Technology* **32**, 317-326. [3] Berthelin *et al.* (2000) *Environmental Mineralogy* **2**, 7-25.

Mineralogy and geochemistry of Neogene mudrocks from Khuzam and Durri formations in southern Egypt

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Mineralogy and geochemistry of the Neogene mudrocks of the Khuzam and Durri formations at Southern Wadi Qena area have been investigated. X-ray diffraction analysis of the bulk samples for Khuzam and Durri Neogene mudrocks revealed the presence of clay (smectite, mica "illite" and kaolinite) and non-clay (quartz, calcite, dolomite, feldspar, anhydrite, halite and hematite) minerals. Little variation in the amount of these clay minerals throughout the Khuzam and Durri Formations proved that the mudstone beds are thought to have derived essentially from same sources at Red Sea High Hills. Kaolinite and illite may have neoformed after smectite, the main clay mineral in the area, contemporaneously with accumulation of Qena lake sediments. Both major oxides and trace elements were analyzed for 40 mudrock samples from the studied area. The unstandardised discriminant function scores, F1 and F1 for major elements of the Neogene sediments under study were calculated according to Roser and Korch (1988) method. They were plotted on the diagram, following the boundaries (P1- P4) proposed by those authors. Plotting of the studied samples revealed that the intermediate igneous rocks were the main source of these mudrocks that were derived mainly from the Red Sea mountains. The study revealed also that the trace elements exhibit no vertical and/or lateral variations, indicating monotonous source.

Geochemistry of the Zn-Pb-Cu-(Ag)-(Au) epithermal deposits from San José (SE Spain)

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The San José Zn-Pb-Cu-(Ag-Au) vein systems, previously described as low-sulfidation [1], are located in the Cabo de Gata Volcanic Field (SE Spain). These deposits comprise mainly base metal bearing sulfide/sulfosalts quartz veins, while disseminated pyrite with small quantities of gold appear in areas of vuggy silica alteration.

Wallrock alteration includes silicification, advanced argillic, argillic and propylitic zones. Very abundant, penetrative, stockwork-like Fe-Al sulfate veins are found in the argillic and advanced argillic alteration, but ore veins do not show a clear relationship with the alteration zone. Mass balance using the isocone method reveals a gradual leaching of most of the elements (except silica) in the highly altered volcanic rocks involving a generalized loss of mass and an increase in the content of some metallic elements (Zn, Pb, Cu) in the less altered zones.

Vein sulfides show a similar or slightly heavier sulfur signature ($\delta^{34}\text{S}$: 6-12‰) compared to the dominant volcanic signature of the zone ($\delta^{34}\text{S}$: 1-7‰ [1]), suggesting a magmatic source but with possible incorporation of sea water sulfate via inorganic reduction. Such magmatic input could also be related to the gold mineralization. The barite signature ($\delta^{34}\text{S}$: 19-21‰) also supports sea water involvement. Pyrite in silicification shows depleted sulfur ($\delta^{34}\text{S}$: 2-6‰) perhaps as product of the disproportionation of magmatic SO_2 which produced the acid alteration. Abundant alunite-jarosite has light sulphur ($\delta^{34}\text{S}$: 4-10‰), but its abundance and occurrence rule out a simple supergene origin. Meanwhile, oxygen isotopes in quartz ($\delta^{18}\text{O}$: 8-18‰) indicate the likely involvement of magmatic and non-magmatic fluids in ore mineralization.

The field, mineralogical and geochemical data suggest a complex mineralization history in the San José area, with evidence of both low and high sulfidation hydrothermal systems and the involvement of magmatic and seawater fluids.

[1] Arribas *et al.* (1995) *Econ. Geol.* **90**, 795-822.

Study of sediments and polluted waste piles in Mazarrón (SE Spain)

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This work studies the pollution level of sediments and waste pile samples from the mining area of Mazarrón (SE Spain). The total concentration of trace elements was screened in the field by a portable x-Ray Fluorescence (XRF) obtaining very high values for As, Pb and Zn, with maximum concentrations higher than 100 g kg⁻¹ of Zn, 34 g kg⁻¹ of Pb and around 2000 mg kg⁻¹ of As. A toxicity bioassay with lettuce (*Lactuca sativa L*) was used to assess the level of pollution. The assay was performed with extracts obtained from a soil:water mixture (ratio 1:5), and with serial dilutions (1:1, 1:2, 1:4, 1:8, 1:16, 1:32, 1:64 and 1:128) to obtain the EC50 (Effective Concentration that reduces the response of the organism by 50% compared to the control). The water-soluble concentrations were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The test consisted of germinating the lettuce seeds in the different solutions obtained, for a period of 120 hours at constant temperature. The parameters evaluated were: Seed Germination (SG), Root Elongation (RE), and Root Necrosis (RN) and the results were expressed as a percentage of reduction in relation to the control (distilled water).

The results indicated that most of the samples had a high degree of toxicity, with very high RN values even at dilutions of 1:16 and 1:32. The SG and RE also indicated a strong reduction in relation to the control in most of the samples. The EC50 values indicated that in many cases the As and heavy metals concentrations in the soil solutions were highly toxic. This study therefore shows that urgent remediation measures are required to minimize the environmental risk and avoid the dispersion of the pollution to adjacent areas.

Hg isotopic composition in lichens: A new tool to monitor air quality and pollution sources

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Lichens are filters of atmospheric particulate and gaseous matter and well-known passive bio-monitors of air quality. Trace metal concentrations and isotopic ratios (Pb) contained in lichens were widely used to quantify, discriminate and monitor atmospheric emissions or depositions. Hg is an emerging isotope system and promising for our understanding of its biogeochemical cycle. Moreover, mass dependent (MDF) and non-mass dependent fractionation (NMF) of Hg isotopes can be used for source tracing of atmospheric mercury. Our goal is to show the potential of Hg isotopes measured in lichens to assess atmospheric sources and depositions, and the overall air quality at the local and global scale.

Lichens (43 samples from 20 sampling points) were sampled over a 7 year time span (2001-03-06-08) within and around a 300 000 inhabitants city in NE of France in a 15 km radius. The main wind directions are SW and NE. Except for one sampling point (see below), all lichens show a range of Hg concentrations from 80 to 200 ng.g⁻¹ and of $\delta^{202}\text{Hg}$ (relative to NIST 3133) from -2 to -0.6 ‰, both homogeneous from year to year at a given locality. The isotopic composition varies systematically along a SW-NE section across the studied area, with $\delta^{202}\text{Hg}$ lower in rural sites (-2‰) and reaching -0.6‰ in the city centre.

We measured significant NMF in all samples, with negative $\Delta^{199-201}\text{Hg}$ (-0.6 to -0.2‰). These cap-delta values also show a gradient along the SW-NE section, the more negative anomalies being in the outer part of the city. The data suggest a progressive contribution of direct anthropogenic sources from rural/sub-urban to urban sites. Lichens sampled in the SE corner of the area display a uniform isotopic composition ($\delta^{202}\text{Hg} = -1.00 \pm 0.25\text{‰}$, 2SD n=5 and $\Delta^{199-201}\text{Hg} = -0.45 \pm 0.20\text{‰}$, 2SD n=5), within the overall measured range. In contrast, all lichens sampled in one locality of the NW corner (15 Km from downtown) have higher [Hg] (400 ng.g⁻¹) and positive $\delta^{202}\text{Hg}$ (+1.4 \pm 0.2‰ 2SD, n=4). This could be attributable to the presence a nearby iron mining sites.

Present emission of methane, ethane and propane from Earth's degassing

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Contemporary geological sources of methane, including gas manifestations and microseepage from petroliferous (sedimentary) and geothermal areas, are the second most important natural emission of this gas to the troposphere (~53 Tg/y; [1]), after wetlands. It represents almost 10% of total methane emission into the atmosphere. Geo-methane emissions are now considered as a new class of greenhouse-gas source for the European (EMEP/COIRINAIR) and US (EPA) emission inventories. Global geo-methane emission estimates have recently been supported by top-down analysis based on the newly derived atmospheric fossil methane (radiocarbon-free) fraction of ~30% [1]. Six source categories must be considered: mud volcanoes, gas seeps (independent of mud volcanism), microseepage (diffuse exhalation from soil in petroleum basins), submarine seepage, geothermal (non-volcanic) manifestations and volcanoes. Marine seepage and microseepage are the largest sources (~20 and 10-25 Tg/y, respectively) and their uncertainties need to be reduced.

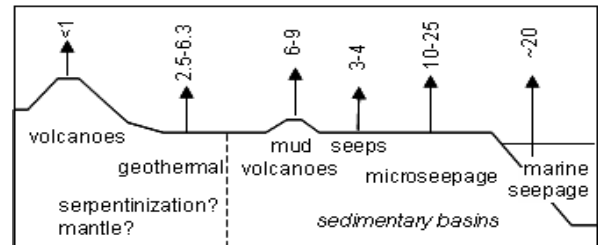


Figure 1: Global geo-CH₄ emission estimates (Tg CH₄/y).

Recently, a robust data-set consisting of methane, ethane and propane concentration in surface gas manifestations from 238 sites throughout the world, allowed to estimate a global geological output of ethane and propane in the order of 2-4 Tg y⁻¹ and 1-2.4 Tg y⁻¹, respectively [2], i.e., Earth's degassing accounts for at least 17% and 10% of total ethane and propane emissions. Geologic seepage is therefore important not only for the greenhouse gas budget but also for emission of ozone precursors and photochemical pollutants. The atmospheric budget of hydrocarbons is not independent of geophysical processes of the solid Earth and planet degassing.

[1] Etiope *et al.* (2008) *Res. Geoph. Lett.* **35**, L09307.

[2] Etiope & Ciccioli (2009) *Science* **323**, 5913, 478.

Detecting total dissolved sulfide anomalies in marine sediments using XRF core scanner

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X-Ray fluorescence core scanning (XRF-CS) allows the rapid, non-destructive, and semi-quantitative determination of high-resolution geochemical profiles along split sections of marine sediment cores. Over the last decade, XRF-CS has provided a wealth of information on past changes in the accumulation of biogenic and terrigenous material in sediment records.

Here, we show that XRF-CS can be used to detect Total Dissolved Sulfide anomalies in sediment cores. A series of cores collected at cold seeps from the Niger Delta area (as part of a joint project between TOTAL and IFREMER; ERIG-3D) was analysed on-board by XRF-CS (Aavatech), immediately upon core opening. Prior to analysis, sediment surfaces were covered with a thin ultralene film (4µm thick) to prevent contamination, oxidation and drying. Selected sediment samples were also processed for quantitative WD-XRF (both oxidised and total sulfur contents) and pore water analyses: Total Dissolved Sulfide contents (by colorimetry, on board) and dissolved sulfate (ion chromatography).

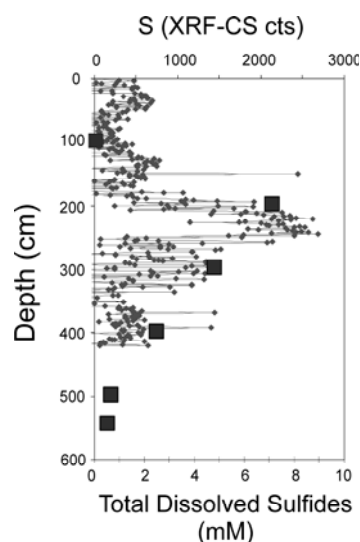


Figure 1: Example of the correlation between XRF-core scanner S and pore water TDS (infilled squares) data versus depth.

Taken together, the XRF-CS, WD-XRF and pore water data indicate that the S signal measured by XRF-CS in our studied cores is mainly driven by the presence of total dissolved sulfides in pore waters. The potential of XRF core scanning for detecting pore water signals in marine sediment cores will be further discussed.

Copper speciation and partitioning between vapor and liquid phases in sulphuric solution: An XAS study

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To understand the role of sulphur in copper transport and vapour-liquid partitioning in hydrothermal fluids, the solubility of copper(I) sulphide (Cu_2S) and the structure of copper species in hydrothermal sulphuric solutions at 25-600°C and 180-600 bar were measured using the synchrotron X-ray absorption spectroscopic (XAS) techniques. This study provides the first *in situ* evidence of solubility of copper sulphides and structure the predominant copper species in sulphuric fluids at high temperature. We find that either linear bisulfide complexes (e.g., $[\text{HS-Cu-SH}]^-$ or $[\text{H}_2\text{O-Cu-HS}]^0$) predominate in alkaline solutions, which indicates that aqueous Cu-S complexing at high temperature and pressure is simpler than ambient conditions where various types of multi-nuclear species have been identified (Helz *et al.* [1]).

The Cu_2S solubility we observed in this study show remarkable agreement with solubility calculations using available thermodynamic data for copper hydrosulphide complexes (mainly $\text{Cu}(\text{HS})_2$) from Mountain & Seward [2] and Akinfiev & Zotov [3], suggesting those data are reasonable and can be used for modelling of copper transport in hydrothermal sulphuric fluids.

The phase separation data from this study shows that significant amount of copper can be partitioned to vapour phase, with apparent partitioning coefficients around 0.3-0.8. However, these experimental data are still not sufficient to explain the preferential partition of copper into the vapour phase observed in many natural fluid inclusions from porphyry copper deposits.

[1] Helz *et al.* (1993) *Geochim. Cosmochim. Acta* **57**, 15-25.

[2] Mountain & Seward (1999) *Geochim. Cosmochim. Acta* **63**, 11-29. [3] Akinfiev & Zotov (2001) *Geochem. Int.* **39**, 990-1006.

Can we use the mineralogical and chemical composition of medieval slags to understand historical smelting technologies?

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Slags from the Pb/Ag medieval (XIVth century) smelting plant located at Bohutín, Příbram district, Czech Republic, were studied from the mineralogical and geochemical points of view. Two types of slags were distinguished: (i) quenched slags formed mainly by Pb-rich glass and unmelted residual grains of SiO₂ and feldspars and (ii) crystalline slags mainly composed of Fe-rich olivine (fayalite) and glass. From the chemical point of view, slags exhibit low concentrations of CaO (up to 5.3 wt%) reflecting a lack of addition of CaCO₃ as a melting agent (this flux is routinely applied in modern Pb metallurgy) [1, 2]. High concentrations of PbO (up to 34.4 wt%) indicate a low efficiency of the medieval extraction process. The mean log viscosity value of slags, using the model of Giordano *et al.* [3] for 1200°C, varies from 1.652 to 2.499 Pa s (mean: 2.119 Pa s). Such high viscosities indicate either high SiO₂ content (which can be related to unmelted quartz grains) or low metal extraction and lower ability to flow out of the furnace. The projection of the bulk composition of slags onto the SiO₂-PbO-FeO ternary system was used for temperature estimates of slag formation, being probably between 800-1200°C. Better temperature estimates are impossible because of the lack of experimental data on complex PbO-rich systems chemically similar to medieval slags. The morphology of olivine crystals was used to estimate the cooling rate of the melt, which for some slags indicates > 1450°C/h. However, known cooling regimes in natural melts (mainly forsterite-based) cannot be fully applied to fayalite-dominated slag melts [2].

[1] Ettler *et al.* (2000) *C. R. Acad. Sci. Ila* **331**, 245-250.

[2] Ettler *et al.* (2009) *Archaeometry* **51**, (in press) doi: 10.1111/j.1475-4754.2008.00455.x). [3] Giordano *et al.* (2006) *Chemical Geology* **229**, 42-56.

What is extreme? Methanotrophy at pH 1 or without oxygen?

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Typically, either hot, very acidic or alkaline habitats are considered 'extreme', but energy limitation may make the life of organisms just as difficult. Here we compare two groups of methanotrophs that we have enriched and/or isolated in our laboratory under unusual conditions.

Members of the verrucomicrobial genus *Methylacidiphilum* have recently been isolated from three highly acidic, geothermal areas independently [1]. They grow aerobically at 37-65°C and at pH 0.8-6, with a minimum generation time of 10 h. In addition to their pH and temperature optimum, they markedly differ from proteobacterial methanotrophs in having ≥3 copies of pMMO genes and no extensive internal membrane system. Yet, major metabolic pathways appear similar.

Another new group of methanotrophic bacteria was enriched by incubating freshwater sediments anaerobically with constant supply of methane and nitrite. The enrichment was dominated (up to 80 %) by bacteria of the 'NC10' phylum [2]. Growth was very slow, with a doubling time in the order of 1-2 weeks. The enrichment culture oxidized methane and reduced nitrite stoichiometrically to CO₂ and N₂. In order to understand the physiology and ecological niche of these anaerobic methanotrophs, we carried out metagenomic, proteomic and physiological studies. Main metabolic pathways could be partially elucidated by the analysis of the assembled genome of the dominant 'NC10' bacterium and by enzyme assays. Although these bacteria also live under anaerobic conditions, their biochemical pathways are entirely different from marine microbes coupling methane oxidation to sulfate reduction [3].

We hypothesize that, owing to the difficulty in activating methane under anaerobic conditions, microbial methane oxidation is more challenging under anaerobic, mesophilic conditions than aerobically at low pH and high temperature.

[1] Semrau *et al.* (2008) *Trends in Microbiology* **16**, 190-193.

[2] Raghoebarsing *et al.* (2006) *Nature* **440**, 918-921.

[3] Hallam *et al.* (2004) *Science* **305**, 1457-1462.

Effects of microstructure and secondary phases on the dissolution of Fe-rich sphalerite

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Mining activities on sulfured ores transfer large amounts of rocks to waste heaps and thus into an oxidizing environment. Weathering of these deposited sulfides often result in acid mine drainage with the production of sulfuric acid and the release high concentration of metals into ground and surface waters. Accordingly, a large number of experimental dissolution studies on various sulfide minerals have been conducted in the past decades including both chemical and microbial leaching under a wide range of oxidizing conditions. Applying measured rates to another system requires knowledge about the mechanisms of dissolution and the *reactive* surface area. However, reactivity is considerably influenced by the microstructure (exsolution, twin planes, stacking sequences) and the defects (vacancies, dislocations, grain boundaries) present. Surprisingly, the influence of the microstructure on the dissolution is rarely addressed. Furthermore, hazardous element release is not only controlled by the reactivity of the primary sulfides but also by the formation of a secondary mineral assemblage. Many of the newly formed phases (oxides, hydroxides, elemental sulfur, sulfates) exhibit small grain sizes, which affects their stability as well as their adsorption capacity. The secondary phases can directly (as coating) or indirectly (adsorption, solubility) influence the dissolution kinetic of the primary sulfide.

Natural iron-rich sphalerites are well known for their wealth of microstructure including stacking faults, twin boundaries and oscillatory zoning, usually combined with elevated trace element concentrations. For this study, sphalerites of two localities (Hungary, Kosovo) with various iron contents have been characterized using TEM for the microstructure, EMPA and LA-ICP-MS for major and trace element compositions as well as SEM and AFM to document surface evolution. Batch dissolution experiments are performed using single crystals as well as powders under conditions that facilitate the precipitation of secondary phases. The influence of microstructure and secondary phases on the dissolution of sphalerite and the solution chemistry will be demonstrated and discussed.

Was the inventory of the marine fixed nitrogen twice as large at the LGM compared to the Holocene?

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Throughout the last deglaciation, the marine inventory of fixed nitrogen was altered by varying rates of water column denitrification, sediment denitrification and nitrogen fixation. Some studies have argued that this inventory decreased by about 30% between the last glacial maximum (LGM) and the Holocene primarily due to water column denitrification having nearly doubled across this period [1, 2]. Such variations of the fixed nitrogen inventory likely will have changed the magnitude and spatial pattern of oceanic productivity and may have contributed to the concomitant changes in atmospheric CO₂. Past variations of the fixed nitrogen inventory have been evaluated mostly through stable nitrogen isotope analyses of organic matter in sediment cores ($\delta^{15}\text{N}$). However, the interpretation of $\delta^{15}\text{N}$ variations is challenging because it is difficult to determine which part of the measured $\delta^{15}\text{N}$ signal is of local origin, e.g. due to change in the degree of fixed nitrate consumption, and which part is of basin-scale to global nature, e.g. reflecting a change of the mean oceanic $\delta^{15}\text{N}$ value due to global-scale changes in the fixed nitrogen inventory.

Here an oceanic geochemical multi-basin box model is used to investigate the inventory of the fixed nitrogen during the last deglaciation. We spatially extend the single-basin box model of Deutsch *et al.* [3] by adding boxes reflecting the Indo-Pacific, the Atlantic and the Southern Ocean.

Several deglaciation scenarios are simulated considering different water column and sediment denitrification forcings as well as various feedbacks between nitrate concentration and denitrification or nitrogen fixation. Simulation results that match the closest the $\delta^{15}\text{N}$ paleoceanographic records in each basin are selected and the LGM fixed nitrogen inventory is evaluated given the evolutions of the sink and source rates.

- [1] Ganeshram *et al.* (2000) *Paleoceanography* **15** (4) 361-376. [2] Altabet *et al.* (1995) *Nature* **373**, 506-509. [3] Deutsch *et al.* (2004) *Global Biogeochem. Cycles* **18** (4).

Surface passivation does not impede biotransformation of Fe oxides by *Shewanella oneidensis*

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At later stages of microbial reduction experiments reduction rates are often observed to drop, even when Fe(III) sources are not depleted and reducing conditions prevail. This study investigates, whether surface passivation, i.e. the formation of Fe(II)-rich coatings on the original Fe(III) particles, might be a limiting factor in dissimilatory Fe reduction.

We performed incubation experiments with *Shewanella oneidensis* using lactate as the carbon source and (i) goethite, (ii) poorly crystalline goethite, (iii) a mixture of goethite and ricefield soil material as electron acceptors. Solids were examined by XRD, Fe-XANES and XPS to determine extent, arrangement, and mineralogy of newly formed Fe(II) minerals. XRD was able to identify vivianite after incubation of both types of goethite. Fe-XANES suggests that metavivianite and Fe(II)-lactate were formed as well.

To investigate the spatial Fe(II) distribution we collected maps at different energies (pre-edge: 7110eV; high energy: 7200 eV; whiteline Fe(II): 7127.5 eV, whiteline Fe(III): 7131.5eV) and maps of XANES spectra across individual particles. While many finegrained Fe(III) particles survived incubation, we observed that most of the larger particles (5-100µm) have been completely transformed to or newly formed as Fe(II) phases. Within the spatial resolution of ~1µm XANES spectra and major element distribution of all investigated bio-reduced Fe(II) particles did not differ between core and rim. By XPS, we detected a still significant contribution of Fe(III) in the topmost nanometers of the surface of all incubated samples. We conclude that surface passivation did not occur at the given experimental conditions.

Isotope domain mapping of ⁸⁷Sr/⁸⁶Sr biosphere variation, UK

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The potential of ⁸⁷Sr/⁸⁶Sr isotope composition to the tracking and origin of material, whether it is humans, animals, water or wine can only be fully realised if high-quality reference data sets are available against which to compare the unknowns. This is currently not the case. Despite the rapid increase in ⁸⁷Sr/⁸⁶Sr-based provenance studies of biosphere materials there are no well documented maps available. Most researchers resort to generating reference maps from a variety of geological datasets and the analysis of sparse 'environmental' samples. A major reason for this lack of reference material is the investment needed to undertake systematic sampling and analysis over large areas. A further problem is associated with choice of proxy material, as organisms differ in their habitat and exploitation of resources. In this paper various approaches to isotope biosphere sampling are considered, some of the problems are assessed, the precision required for the study of human populations is discussed and a first attempt is made to condense all of the available information into an 'isotope package' map. The study details work undertaken on the Island of Skye, Scotland where the complexity of geological and isotope data is reduced into five main ⁸⁷Sr/⁸⁶Sr packages, and goes on to considered the approach to producing a biosphere map for the UK.

New internally consistent data and activity composition models for S-bearing phases, and application to thermodynamic modelling of mafic greenschist facies rocks from the St. Ives gold camp, Western Australia

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Sulphur is ubiquitous in many ore-forming environments and plays a critical role in that it combines with with metals of economic interest in aqueous species and minerals. Prediction of the relative stability of S-bearing phases and aqueous species is a valuable tool in the formulation of conceptual models for ore formation. However, sulphur-bearing phases have proved difficult to incorporate rigorously into thermodynamic models, because of non-ideal mixing relationships and the difficulty of defining equations of state for materials with multiple phase changes.

Here we present an augmented version of the Holland and Powell (1998) internally consistent dataset [1] that includes common S-bearing phases. A thermodynamic description of the troilite-pyrrhotite solid solution series has been formulated that agrees well with experimental heat capacity data and studies of activity-composition relationships.

The dataset, which is incorporated into the thermodynamic modelling software THERMOCALC, has been used to construct pseudosections, which are phase diagrams for a specific bulk composition, for rocks with bulk compositions similar to those that host gold at the St. Ives gold camp, Western Australia. The results demonstrate that observed accessory phase assemblages, which have been attributed to mixing between mixing between oxidised and reduced fluids, are also consistent with gradients in temperature, fluid composition, and extent of water:rock interaction.

[1] Holland & Powell (1998) *J. Met. Geol* **16**, 309-343/

(U-Th)/He Magnetite dating of exhumed serpentized mantle: A case study from the Tasna Ocean-Continent Transition, SE Switzerland

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The development of magnetite (U-Th)/He dating offers unprecedented potential for direct dating of serpentinization and mantle exhumation. While mantle rocks do not contain mineral phases typically used in geo- and thermochronometric studies, magnetite is ubiquitous as it forms from the breakdown of olivine during serpentinization. It has been shown in basaltic rocks that magnetite can be dated reliably by (U-Th)/He thermochronometry and is characterized by a He closure temperature of ~250°C. The novel application of magnetite (U-Th)/He thermochronometry on exhumed serpentized mantle would provide critical age constraints on continental breakup during rifting of magma-poor continental margins. Serpentinization of exhumed mantle rocks has been proposed to occur during the final phase of rifting during continental break. Direct dating of mantle exhumation and serpentinization, therefore, would not only constrain the timing of continental rupture, but also elucidate the duration of tectonic processes leading from rifting and continental attenuation to continental break-up.

The ocean-continent transition (OCT) preserved in the Tasna nappe of SE Switzerland provides an ideal area to undertake a systematic study on the viability of magnetite (U-Th)/He thermochronometry of exhumed sublithospheric mantle. The Tasna OCT is comprised of a sliver of highly attenuated continental basement juxtaposed against serpentized mantle peridotites along a low-angle normal fault system and capped by Cretaceous to Eocene post-rift sediments. Magnetite (U-Th)/He data from the serpentized mantle combined with zircon (U-Th)/He data from the thin wedge of continental basement across the Tasna OCT will provide new constraints on mantle exhumation and give insight to the sequence and timing of processes that occur in a more general sense at OCTs in magma-poor rift margins.

Exploiting synergies in molecular structures, isotopic signatures and faunal evidence to enhance archaeological interpretations

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The paucity of finds in the archaeological record at the earliest stages of development of human civilisations make it essential to combine multiple lines of evidence to achieve robust reconstructions. The past 3 decades have seen major developments in the use of organic residues from a wide variety of archaeological artifacts and deposits to enhance our knowledge of the use of particular finds, evidence of technological activities and the exploitation of a wide range of natural resources. Considerable interest has focussed on the chemical analysis of organic residues preserved in pottery vessels involved in the processing of animal and plant products, i.e. 'cooking' vessels. Such residues provide information relating to the specific functions of vessels and, more significantly, the wider aspects of settlement and regional economy and diet. In this respect food residues surviving in pottery vessels are highly complementary to other dietary indicators, particularly faunal remains.

This presentation will discuss the analytical approaches to the investigation of the major class of organic residue observed in prehistoric pottery, namely degraded animal fats. Although the major components detected, i.e. *n*-alkanoic acids and other acyl lipids, are rather non-specific biomarkers it will be shown how compound-specific stable isotope values greatly enhance their diagnostic potential. Examples will be given which demonstrate classifications of species origins based on the $\delta^{13}\text{C}$ values of $\text{C}_{16:0}$ and $\text{C}_{18:0}$ alkanolic acids as a result of them recording the physiological and metabolic differences between the major domesticates. An entirely new approach will be presented which shows how compound-specific carbon and deuterium isotope values of the same alkanolic acids can be used in tandem, exploiting metabolic and seasonality effects, to further refine assignments. In all cases the interpretations based on molecular and stable isotope signatures are supported by detailed assessments of faunal assemblages to provide hitherto unobtainable insights into the early exploitation of bovines and equids for their 'secondary products' in Europe, the Near East and Eurasia.

Peculiarities of Pd-Pb-Bi system minerals

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Samples and probes of Cu-Ni sulphide ores from Noril'sk deposits have been studied using SEM. New data on polarite and plumbopalladinite compositions are received. It leads to the reviewing of phase relationships in the system Pd-Pb-Bi. Minerals of this system, polarite [Pd(Pb,Bi)], zvyagintsevite [Pd₃Pb], plumbopalladinite [Pd₃Pb₂], sobolevskite [PdBi], and froodite [PdBi₂] normally do not form the separate grains. They are included in complex intergrowths with other Platinum-Group Minerals as small grains (up to first tens microns). Although Pd-Pb-Bi minerals are described in many publications, some questions remain still open: 1) the limits of isomorphous replacement Pb-Bi in polarite; 2) the problem of ordered members of PdBi-PdBi isomorphous series; 3) the composition of plumbopalladinite; 4) polarite – sobolevskite relationships. Data on polarite composition show that near complete series PdBi-PdPb exists. However, according to the detail study of phases synthesized in PdPb-PdBi with x-ray diffraction, SEM+EDD along this series there are some ordered compounds with stoichiometric formula coefficients (Pd:Pb:Bi). The similar observations are determined for minerals too. Crystallochemical characteristics of PdBi and PdPb allow distinguishing new minerals in the polarite series. The composition of polarite depends on the mineral association. For example, more Bi-rich polarite is characteristic for associations, containing Sn- or As- bearing PGM (i.e. stannopalladinite, palarstanide, atokite, majakite, sperryllite etc.).

The composition of plumboipalladinite very often shows the deviation from stoichiometry 3:2. SEM+EDD study showed that plumbopalladinite 'non-stoichiometry' is caused by tiny inclusions (n:10nm – n μm) of zvyagintsevite, Pd₃Pb, polarite Pd(Pb,Bi), urvantsevite, Pd(Pb,Bi)₂, froodite, PdBi₂, and phase «Pd₂Pb». Sometimes plumbopalladinite from Noril'sk deposits with composition Pd₃Pb₂ is presented by very tiny intergrowths of two mineral phases - (Pd₂Pb + PdPb) or (Pd₃Pb + PdPb). Therefore it is necessary to review the composition of every 'plumbopalladinite' find.

***In situ* measurement of Hf isotopes in rutile by LA-MC-ICPMS**

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The measurement of hafnium (Hf) isotopes in accessory minerals such as zircon is now a well-established geochemical tool for tracing input from different crustal and mantle reservoirs. Recent studies have pioneered the *in situ* measurement of Hf isotopes in rutile, and demonstrated an intriguingly large range in $^{176}\text{Hf}/^{177}\text{Hf}$ values for rutile from MARID and eclogitic xenoliths [1, 2]. However, with one to two orders of magnitude less Hf than zircon, rutile presents a number of technical challenges for *in situ* measurement of Hf isotopes. We present the first rigorous assessment of the accuracy and precision with which Hf isotopes can be measured *in situ* for rutile, along with a revised LA-MC-ICPMS protocol adapted to suit this low-Hf mineral.

In order to maximise accuracy and precision, well-determined baselines are critical, and can be achieved by a combination of long baseline measurement times and averaging across an analytical session. Another key factor is the regular analysis of a synthetic rutile doped with c.5000ppm Hf to monitor, and if necessary externally correct for, mass bias. It can be demonstrated that although mass bias does change perfectly linearly with time, the low precision with which mass bias coefficients can be determined for rutile induces a much greater degree of scatter in apparent mass bias than the real variation, in some cases negating the advantages of internally correcting for mass bias.

Accuracy of the technique is confirmed by results for two rutiles for which the $^{176}\text{Hf}/^{177}\text{Hf}$ is known by independent means. Analyses of synthetic rutiles doped with Hf do not show a systematic offset in measured $^{176}\text{Hf}/^{177}\text{Hf}$ with varying Ti/Hf, as previously proposed for solution MC-ICPMS [3]. Although precision is lower than for zircon by a factor of 5 to 10, it is sufficient to distinguish between rutile from different samples. Zircon and rutile from a single metamorphic sample have also been shown to record different $^{176}\text{Hf}/^{177}\text{Hf}$ signatures, demonstrating that Hf isotopes in rutile provide an important complementary tool for deciphering metamorphic histories.

[1] Choukroun *et al.* (2005) *Geology* **33**, 45-48. [2] Aulbach *et al.* (2008) *Nature Geoscience* **1**, 468-472. [3] Münker *et al.* (2001) *Geochemistry Geophysics Geosystems* **2**, 2001GC000183.

Small scale mining and heavy metals pollution of agricultural soils: The case of Ishiagu mining district, South Eastern Nigeria

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Methods

This research assesses the distribution pattern of Pb, Zn, Cu, Cd, Co and Ni in agricultural soils in the Mining District of Ishiagu. The pollution level of the soils was also evaluated, based on existing guidelines. 26 samples of surface soil picked at the interval of about 1000m was digested by use of aqua regia and analyzed by use of AAS for Pb, Zn, Cu, Cd, Co and Ni. Detailed description of the methods is discussed in the paper.

Results

The contour maps, each showing the distribution of individual metals were generated. After evaluation, pollution map for the individual polluting metal were also made.

The case of pollution of soils in parts of Ishiagu by Pb, Zn and Cd was established. This is attributable to releases from mine dumps, concealed Pb-Zn lodes and the bedrock which get exposed during mining activities. The bedrock which comprises basic intrusive and dark coloured shales contains high concentrations of these metals [1]. Fertiliser application in soils is minimal and thus contributes very little metal to soils. Their accumulation in soils results from the clayey and the ferrallitic nature of the soils [1, 2], and the presence of carbonate materials [3-5].

[1] Olade (1987) in Hutchinson (ed.) *Lead, Mercury, Cadmium and Arsenic in the Environment*, pp303-313. [2] Sparks (2005) *Elements* **V3**, 193-197. [3] Ferguson (1990) *The heavy Elements: Chemistry, Environmental Impact and Health Effects*, p614. [4] Kabata-Pendias & Pendias (1984) *Trace elements in soils and plants*, 3rd edition, p315. [5] Adriano (1986) *Trace Elements in Terrestrial Environment*, p533.