

Accretion, chemical evolution, and differentiation of the terrestrial planets

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Terrestrial planets grow by repeated collisions in a swarm of ~10 km-scale planetesimals and lunar- to Mars-mass embryos. N-body modeling of this process has successfully reproduced many aspects of the Solar System's terrestrial planets [eg. 1,2], although reconciling all of the available evidence is still an outstanding problem [3]. We will give an overview of the current state-of-the-art in the modeling of terrestrial planet formation, with a specific focus on its implications for the chemical evolution and differentiation of terrestrial planets.

Significant radial mixing can occur during terrestrial planet formation, delivering volatile elements into the terrestrial planet region. Large impacts, which are common during the final stages of terrestrial planet formation, can lead to volatile loss. Recent work that combines N-body accretion simulations with a nebula condensation model finds that elements such as Na, P, and S are overabundant in simulated planets, but become much more consistent with Earth's abundances when a simple model of impact heating and volatile loss is included [4]. This may have important implications for the Earth's initial water budget.

Radiogenic and impact heating leads to melting and differentiation of the growing planets, with iron and siderophile elements separating from rocky material and segregating into the core. In addition, many of the large embryos impacting the planets are likely to be differentiated themselves. The Hf-W isotopic system provides a way to understand and date this process, but is subject to some uncertainties, namely the degree to which the cores of the impacting embryos are able to mix and equilibrate with the mantle of the growing planet [5]. Analyzing N-body accretion simulations to track the Hf-W isotopic evolution of the growing planets suggests that a significant degree of equilibration during impacts is necessary to match the Hf-W isotopic signatures of Earth [6]. Constraining Mars' differentiation history is more difficult, although it is clear that it differentiated before the Earth [7].

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Biogeochemistry of electron transfer at the iron oxide-solution interface in sediments

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Iron oxides are ubiquitous in sediments, aquifers and soils, where Fe(II)/Fe(III) oxidation/reduction cycles couple biotic and abiotic processes. Mixed-valence iron oxides are involved in the degradation of organic matter, nutrients and pollutants and also the adsorption, retention and mobilisation of numerous substances. Due to these diverse interactions, the iron cycle is intrinsic to the water quality of lakes, coastal waters and groundwater.

Currently there still remain surprisingly large gaps in our understanding of the redox transformation reactions of iron oxides. The role of microbial electron transfer to iron oxide surfaces is not well understood, and we do not know how electrons migrate and redistribute in the solids, and to which extent Fe(II) catalyses the transformation of different iron oxide minerals.

RNA-SIP, based on tracing ¹³C from labelled acetate into the DNA and RNA of the active microbial community, has been applied to natural iron rich lake sediments. This allows us to identify which iron reducing bacteria are active. By combining this with experiments using labelled Fe-oxides enables the derivation of a complementary picture of which Fe-oxide phases are used and which are formed.

The natural lake sediment studied is characterized by a high fraction of very labile Fe-oxides in the top few cm compared to further down. Part of the explanation could simply be the removal of the labile part by microbial reduction, but experiments have shown that fast interactions between adsorbed Fe(II) and Fe(III)-oxide minerals often promote total recrystallization in pure systems. Experiments using natural lake sediments and synthetic ⁵⁵Fe and ⁵⁷Fe labelled iron oxides and aqueous Fe²⁺ will be able to track the rates and effects of these transformations in natural systems where Fe²⁺ is produced by microbial reduction.

Sediment remediation of metal and metalloid contaminants with reactive amendments

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Reactive amendments optimized for specific (bio)geochemical site conditions offer a promising remediation technology for high-priority contaminants (As, Hg, Se, Pb, Cu) in sediments by sequestration and stabilization in less reactive and less bioaccessible solids. For subaqueous or subsurface sites where physical removal is impractical or prohibitively expensive, *in situ* stabilization must be designed for long-term immobilization in potentially variable biogeochemical and hydrologic conditions. Amendment technologies are particularly promising when combined with other methods such as sediment capping, reactive barriers, or monitored natural attenuation in an overall risk management approach.

In laboratory experiments supported by equilibrium and kinetic modeling, we are investigating mercury (Hg) and arsenic (As) immobilization with Fe-sulfate and Portland cement amendments. Modeling results indicate formation of hydrated Ca-Si-Al and Ca-Fe ettringite phases within 1-7 d. In the Hg system, experimental data are consistent with model results, showing Mg, Ca, and S concentrations at 1 and 7 d that match predictions. Analyses of reaction products up to 30 d by XRD and SEM/EDS confirm model predictions of secondary phase formation. Mercury uptake measurements and sequential extractions show rapid removal from solution and a decrease in extractable Hg with aging time. In the As system, Fe-sulfate and cement amendment was compared with Fe-sulfate-only (low pH) and cement-only (high pH) treatments of sediments aged for up to 1 y. Similar to Hg, As uptake from solution is rapid (>90% in 1-7 d) and extractable As decreases with aging, although there is variability over the time series. Characterization of reaction products by XRD and XAS indicates arsenic sequestration in either ettringite or Fe-sulfate/arsenate secondary phases by arsenic substitution for sulfate, in contrast to Hg(II), which likely substitutes for Ca in secondary phases. Comparison of laboratory results with field-amended sediments suggest that sulfate-cement mixtures are stable for years if pH and redox conditions remain relatively constant.

Effects of oxyanions, natural organic matter, and Fe(III) oxide mineralogy on the formation of Fe(II)-bearing secondary mineralization products resulting from the bioreduction of Fe(III) oxides

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Introduction

The bioreduction of Fe(III) oxides may result in the production of a suite of Fe(II)-bearing secondary mineralization products (Fe(II)SMPs), including magnetite, siderite, vivianite, ferrous hydroxy carbonate (FHC), and green rusts. In an effort to better understand the effects of solution chemistry on the formation of particular Fe(II)SMPs of dissimilatory Fe(III) reduction, we examined the effects of a series of oxyanions and natural organic matter on the bioreduction of Fe(III) oxides by *Shewanella putrefaciens* CN32.

Experimental Methodology

Defined mineral medium containing 75 mM formate and 80 mM Fe(III), in the form of synthetic Fe(III) oxides, was amended with oxyanions or natural organic matter and inoculated with *S. putrefaciens* CN32. Samples were collected for measurement of Fe(II) and characterization of the Fe(II)SMPs by X-ray diffractions, scanning electron microscopy, and ⁵⁷Fe Mössbauer spectroscopy.

Discussion of Results

With no amendment or with the addition of borate, oxalate, or gellan (an extracellular polysaccharide produced by the bacterium *Sphingomonas elodea*) magnetite and FHC formed. The addition of arsenate, molybdate, phosphate, silicate, tungstate, citrate, humic and fulvic acids, or extracellular polysaccharides from *S. putrefaciens* CN32 resulted in the formation of carbonate green rust.

Ultradeep continental roots and their stranded oceanic remnants: A solution to the geochemical “crustal reservoir” problem?

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High-resolution global seismic tomography (Vs) models reveal high-velocity domains beneath cratonic crust in Africa that extend to depths of 300-400 km and show a distinct contrast with “normal” asthenosphere. These are interpreted as depleted, buoyant Archean roots, metasomatised over time, but remained attached to overlying crust. Such deep roots are impediments to free horizontal convection in the upper mantle. The movement of magmas and other fluids in such regions may be more vertically constrained (shallow lava lamp regime), creating a geodynamic environment enhancing interaction of such magmas with deep mantle domains carrying old “crustal” geochemical signatures. Tomographic models and the new world magnetic-anomaly map show that such high-velocity domains also occur in the Atlantic Ocean basin. They are not confined to the basin margins as predicted for normal oceanic-mantle extensional cooling, but are scattered randomly through the Basin, some significantly distant from the continental margins of South America and Africa. These are interpreted as remnant lithospheric fragments isolated by disruption of the ancient continental regions during rifting, supported by old Os depletion ages from mantle peridotites beneath mid-ocean ridges and oceanic islands. Basaltic magmas erupted near such domains carry geochemical signatures (EM1, EM2) of interaction with refertilised cratonic mantle. Interaction of rising magmas with fragments of ancient lithospheric mantle can explain such geochemical signatures and, while not incompatible with recycling of lithospheric material by deep plumes, obviates the need for complex models in which “lithospheric” geochemical reservoirs are isolated and preserved in the convecting mantle. The inferred presence of disrupted ancient lithospheric roots in ocean basins provides new insights on the mechanisms of continental breakup and mechanical disruption. Such “oceanic” ancient lithospheric domains, coupled with the ultradeep continental roots, suggest that original Archean lithospheric mantle is apparently more extensive, both laterally and vertically, than previously considered.

Is there a link between bedrock metamorphic grade and arsenic concentrations in groundwater?

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A groundwater study in Maine, northeastern USA, reported approximately 30% of domestic well waters with arsenic concentrations greater than 10 $\mu\text{g L}^{-1}$ (n=790). Wells tap groundwater in meta-sedimentary bedrock that exhibits varying degrees of metamorphism; increasing (prograde) metamorphism, and contact metamorphism. As a first step towards understanding the processes governing arsenic release into the fractured bedrock aquifer, this study was initiated to examine the distribution and mineralogy of arsenic in bedrock outcrops along a transect of increasing metamorphism. Results from 48 rock samples, ranging from low-grade slate to higher grade gneiss, showed that 75% of low grade rocks had detectable arsenic (XRF mean As 70 mg kg^{-1}) compared to As detected in only 7% of the high grade rocks (XRF mean As 11 mg kg^{-1}). Previous studies show desulfidation converts pyrite (FeS_2) to pyrrhotite (FeS) with increasing metamorphic grade; these mineral distributions have been confirmed herein with SEM-EDX. In low grade rocks, 74% and 94% of As and S respectively were oxidatively leached indicating pyrite oxidation could be a source for most of the arsenic in groundwater of low grade rocks. However, the As:S ratios in oxidative leachates dramatically increase in high grade rocks, indicating an arsenic mineral association more conducive to arsenic mobilization in highly metamorphosed rocks, despite the lower bulk As concentrations in rocks of this grade. Could arsenic be associated with pyrrhotite, and more likely to be mobilized, in high grade metamorphic rocks? Laser ablation ICP-MS is currently being utilized to investigate the link between arsenic, pyrite and pyrrhotite in rocks of different grades. The geochemical conditions promoting arsenic release from this fractured aquifer are complex. This study aims to contribute new information on arsenic variation in rocks of increasing metamorphic grade, their influence on groundwater chemistry, and guide regulatory authorities in their search for safe water supplies.

Petrological and geochemical evidence for within-plate tectonic origin of some igneous rocks from the Lower Benue rift

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Methods and Results

The igneous rocks in the Lower Benue rift (otherwise, Lower Benue Trough) had been shown to have predominantly alkaline character and formed in an extensional, within-plate setting using mainly petrographic and major-element oxide data [1, 2, 3]. In this study, petrographic and geochemical (major, trace and REE) studies reveal that some volcanic and subvolcanic rocks within the original widths of the rift belong to alkali basalt series, with generally high fractionation indices [$(La / Yb)_N$]; 7.06 to 17.65 for basaltic, and 23.59 to 135.35 for trachytic rocks, as well as strong enrichments in the incompatible elements. The basic sills generally show evidence of alteration reflected in depletions in the more mobile LILE (Rb, K, Ba and Sr) and high Th/Ta ratios.

Discussion of Results

This study corroborates the predominantly alkaline character of igneous rocks in the region [1, 2, 3] and suggests derivation from alkali olivine-basalt magma, generated through low degrees of partial melting of an enriched lithospheric mantle due to an asthenospheric uplift with HIMU signatures, in a within-plate continental rift setting. Coulon *et al.* [4] obtained similar mantle sources, as well as an N-MORB source for rocks from other parts of the rift. The alteration in the rocks is likely an effect of interaction with an aqueous fluid phase and crustal contamination; interaction of the igneous rocks in the rift with an aqueous fluid phase had been suggested [2, 5, 6].

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2D, 3D, and *in situ* STXM in geomicrobiology

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Species-Sensitive Mapping using STXM

Biogeochemical processes such as metal binding and mobilization, (bio-)mineral precipitation and dissolution are often microbially mediated and controlled by chemical micro- or nano-environments with strong geochemical gradients. A fundamental understanding of the underlying mechanisms requires quantitative mapping of relevant organic and inorganic species such as bio-macromolecules, metals and minerals at spatially relevant scales. Scanning transmission X-ray microscopy (STXM) combines the speciation-sensitivity of near edge X-ray absorption fine structure spectroscopy with ~30 nm spatial resolution [1].

CaCO₃ biomineral nucleation on the surface of planktonic cyanobacteria was investigated in 2D STXM experiments. Therefore, the biochemical composition of potential nucleation sites and the mineralogical composition of the precipitates were mapped [2] both dry and *in-situ*. A model of the nucleation mechanism was developed, which involves the fast and reversible adsorption of Ca²⁺ to the extracellular polymers, the precipitation of an intermediate, aragonite-like phase, and eventually the precipitation of calcite. This model was verified in an element-specific 3D STXM angle-scan tomography study [3].

Several other biogeochemical applications of soft X-ray spectromicroscopic species-mapping will be illustrated such as microbial anaerobic Fe-oxidation [4], metal adsorption, and biomineralization within natural river biofilms [5].

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Redox-sensitive trace metals during the Neoproterozoic Oxygenation Event

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The transition to a fully oxygenated Earth surface environment during the late Neoproterozoic involved major changes of climatic, tectonic and biological nature and had profound effects on biogeochemical cycling. An increasingly oxygenated Earth's surface would possibly have led to the ventilation of the deep marine environment and to a build-up in the ocean of the redox-sensitive trace metals that are generally more soluble as oxidised complexes, e.g. Mo and V. Because reductive sequestration of these metals results in authigenic enrichment in oxygen-depleted sedimentary facies, ocean anoxic events can affect the budgets of these biogeochemically significant elements [1]. Hence, investigating the trace metal distribution in Neoproterozoic/Cambrian black shales, when a redox stratified ocean [2] and an oxygenated atmosphere coexisted, can shed light on the development and timing of the Neoproterozoic Oxygenation Event (NOE). In this study, we present high resolution trace metal data, with a focus on Mo, V and Mo/TOC ratios in order to constrain changes in the ocean Mo budget during the Neoproterozoic-Cambrian transition [3]. New data from 6 sections in South China and previously published data, covering the Neoproterozoic-Cambrian transitional interval from about 1000 to 500 Ma are used to constrain the timing of the NOE and its possible links to biological evolution.

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Oxidation state of chromium in ferropericlyase inclusions in lower mantle diamonds determined with micro-XANES measurements

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Redox condition of the Earth's interior is a much-discussed subject these days. The valences of Fe of mineral inclusions in diamond were studied as a possible redox indicator. However, it was found that the valence of Fe in lower mantle minerals is constrained by crystallographic structure. In this study, we focused on oxidation state of Cr in ferropericlyase for searching a proper indicator of oxidation state of lower mantle.

Chromium and Fe K-edge X-ray absorption near-edge structure (XANES) spectra of natural ferropericlyase were measured using X-ray microbeam from a synchrotron radiation source to estimate the valence state of Cr and Fe. These samples were inclusions collected from the lower mantle diamonds. The inclusions were picked up from the host diamonds and buried in epoxy mounts. XANES spectra were recorded in the fluorescence mode at the beamlines BL4A of the Photon Factory, KEK, Japan. Relative content of Cr²⁺, was calculated using the method described by Berry and O'Neill (2004). The obtained results revealed that divalent chromium are present in the materials from the lower mantle and the Cr²⁺ proportion to the total Cr content varied among the samples in the range of 4 to 15%. In this presentation, we will discuss about the redox condition of the lower mantle using valence states of Cr and Fe.

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Preliminary results from a study of coarse airborne particles >2.5µm in Hanoi, Vietnam

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The study aimed to identify and classify coarse airborne particles, especially anthropogenic particles, such as those derived from traffic, domestic fuel combustion, and industry. In 2008, two sampling sites were selected in the congested urban area of Hanoi: site 1 represents a background location; site 2 has the character of a roadside location. Using a passive sampling device (Sigma-2), airborne particles were collected on carbon pads for scanning electron microscopy (SEM), as well as on clear adhesive collection plates suitable for transmitted light microscopy. The sedimentation principle of the passive sampler technique permits investigating particles >2.5µm. Chemical composition, geometry and morphology were determined by computer-aided SEM, combined with single-particle analysis (Genesis, EDAX) and energy-dispersive spectroscopy (EDS). Particles were classified according to their composition and assigned to three classes: anthropogenic, geogenic, and biogenic. Computer-controlled single-particle optical microscopy (IAS) of the adhesive collection plates was applied to measure size and optical density of individual particles. Statistical evaluation of the data allows us to assess the abundance of black, elementary carbon particles, which are suggest to be anthropogenic. As expected, these particles are much more abundant in the samples from the roadside than in those from the background site, which is shielded from major traffic sources. These types of particles sampled at the background site are mostly in the size range 2.5–10µm, indicating that they represent particles that have been transported there from the high-traffic roads.

The surface area, reactivity, and effect on global cycles of riverine transported basaltic suspended load

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Several recent studies have emphasized the significant role of riverine transport of basaltic suspended material to the oceans on global cycles and climate moderation [1, 2]. To further quantify this process, co-existing suspended material and water samples have been collected regularly from 8 catchments in NE Iceland over a four year period. The suspended material in these catchments is similar to that of the host rock, which itself is over 90% basaltic glass in composition. The measured B.E.T. surface area of this material was found to range from 10 to 80 m²/g, with an average value of ~30 m²/g.

The dissolution rates of selected suspended material samples were determined in Si-free artificial surface seawater at 5 and 25° C using batch reactors. Initial B.E.T. normalised dissolution rates are found to be ~2x10⁻¹⁷ and 1x10⁻¹⁶ (mol Si)/cm²/s at 5 and 25° C respectively. These rates are approximately one order of magnitude slower than that of basaltic glass at the same conditions [3]. Nevertheless, these results suggest that between 1% and 10% of the basaltic suspended material will dissolve per year once it arrives in the ocean. Whilst much of this mass will be rapidly incorporated into secondary phases, the combined dissolution of the primary basaltic material coupled with secondary phase precipitation will have a strong influence on the isotopic and trace element composition of the world's oceans.

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The Terminations 1 and 2 as revealed by the record of stable isotopes from the EDML ice core

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The data

Within the European Project for Ice Coring in Antarctica (EPICA) two deep ice cores were recovered. The second one (labelled EDML, total depth 2774m) was drilled in Dronning Maud Land (DML) in the Atlantic sector of Antarctica [1]. It is well dated down to the depth of 2416m with an age of 150 kyrs BP [2]. Stable isotopes (¹⁸O, D) have been measured with depth resolutions of 0.5m and 0.05m, and the deuterium excess values were calculated [3]. The stable isotope records for terminations 1 and 2 (T1, T2) were resampled on common time steps of 50 years. Corrections to the ¹⁸O and D values had to be added to account for surface elevation changes and changing ¹⁸O content of the sea water in the past.

Discussion

The most prominent difference between T1 and T2 is that the Antarctic Cold Reversal (ACR) of T1 has no analogue in T2. With the elevation corrections used in [1] T2 shows a steady increase from -51.5 ‰ to -40 ‰ over a time span of 9 kyrs, whereas T1 displays an increase from -52.5 ‰ to -44 ‰ over 8 kyrs. The influence of the elevation corrections will be discussed, which increase $\delta^{18}\text{O}$ during MIS5.5 and lower it during the glacials. The deuterium excess shows differences towards the end of the terminations, with lower values in and after the ACR during T1. The main driver of these differences lie in the conditions prevailing in the evaporative source areas and of the subsequent transport of the moisture providing snow at the site. We infer that the atmospheric transport and the source area of precipitation or the source temperature were different for T1 and T2.

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The passivation of calcite during the treatment of acid mine drainage. Laboratory experiments

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Column experiments simulating the behavior of passive treatment systems for acid mine drainage have been performed. Synthetic acid solutions (H₂SO₄) containing Fe(III) (400-1500 ppm, pH 2) or Al (100-1000 ppm, pH 2-3) were injected into column reactors packed with calcite grains. Grain size was between 1 and 2 mm and flow rates (6x10⁻⁷ - 10⁻⁶ m/s) were kept constant during the experiments. Aragonite and dolomite were also tested. The columns worked as an efficient barrier for some time, increasing the pH of the circulating solutions to ~7 and removing its metal content. Previous results [1] had already shown that gypsum precipitation coated the carbonate grains and led to the passivation of the system, while metal-oxyhydroxysulfates precipitated towards the center of the pores.

For the Fe(III) system, passivation time decreases with increasing input Fe(III)-SO₄ concentrations, until a minimum asymptotic value is reached. Total Fe(III) retained increases with input concentration when this asymptotic value is reached. Slower flow rates seem to cause an increase in both passivation time and total Fe(III) retained.

For the Al system, passivation time also tends to decrease with larger Al-SO₄ concentrations. Total Al retained also tends to decrease with increasing input concentrations.

Some of the column experiments have been analyzed at regular intervals using synchrotron X-ray microtomography at the ALS (Berkeley, USA). The evolution of pore structure and secondary mineral precipitation (goethite, schwertmannite, gibbsite) at the microscopic scale has been investigated. Mineralogical analyses (synchrotron X-ray microdiffraction) were also performed. The results show the advance of the reaction fronts along the columns, with the formation of the gypsum coatings on the limestone grains and precipitation of metal-oxyhydroxysulfates between the grains. The formation of preferential flow paths in the porous medium has also been observed.

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Redox evolution of volcanic gas through geologic time

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It has been generally assumed that, before ~2.5 Ga, the global flux of reducing volcanic gas ($F_{\Sigma\text{red.v}} = 1/2F_{\text{H}_2} + 2F_{\text{H}_2\text{S}} + 1/2F_{\text{SO}_2} + 1/2F_{\text{CO}} + 2F_{\text{CH}_4}$) was significantly higher than the global oxygen production flux (F_{p,O_2}), resulting in an anoxic atmosphere. However, this was probably not the case.

Considering the estimates made by various researchers for the fluxes of various volcanic gases, I have estimated today's $F_{\Sigma\text{red.v}}$ to be $(0.5 \pm 0.3) \times 10^{12}$ mol/yr, which accounts for only ~5% of today's F_{p,O_2} (~ 10×10^{12} mol/yr); the remaining ~95% of O_2 consumption is carried out by kerogen and Fe^{2+} -bearing minerals during soil formation. I have also estimated F_i , $F_{\Sigma\text{red.v}}$ and F_{p,O_2} values for the Archean world, taking into consideration of the following possibilities: (1) the total land area was much less (e.g., ~5% land and ~95% ocean); (2) the heat flux was ~3 times higher; (3) $f\text{O}_2$ values for the mantle wedges above subduction zones (i.e., FMQ + 2 ± 1 today) were the same as those of the normal mantle (i.e., FMQ - 1 ± 1); (4) pyrrhotite was ubiquitous in magmas and rocks; and (5) the atmospheric $p\text{CO}_2$ was ~100 PAL. (1)-(4) affect F_i and $F_{\Sigma\text{red.v}}$ values, whereas (1) and (5) affect F_{p,O_2} .

The results of computations suggest that the Archean $F_{\Sigma\text{red.v}}$ could have been as high as $\sim 2 \times 10^{12}$ mol/yr, which is about 4 times higher than today's $F_{\Sigma\text{red.v}}$. For comparison, the Archean F_{p,O_2} ranged from ~7 to ~40 ($\times 10^{12}$ mol/yr), depending on whether the deep oceans were oxic or anoxic. These values imply that volcanic gas could not have prevented the oxygenation of the atmosphere within <10 Ma since the emergence of cyanobacteria.

SO_2 is a major volcanic gas today, but it was most likely a very minor specie in Archean volcanic gas; thus it was an unlikely source for the anomalous sulfur isotope signatures in Archean sedimentary rocks.

A dismembered Late-Archean anorthositic to charnockitic suite in the Andriamena greenstone-belt, Madagascar

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The Andriamena greenstone belt includes a late-Archean anorthositic to charnockitic suite, which outcrops in the vicinity of two major chromite deposits, associated with minor harzburgites and orthopyroxenites.

The anorthositic rocks comprise coarse-grained leucogabbros grading to noritic gabbros. Based on the An contents of plagioclase, two groups of gabbroic rocks are defined: a high-An group ranging from An_{90} to An_{60} and a low An-group, with compositions grouped around An_{50} . Mantle characteristics are most strongly displayed in rocks bearing calcic plagioclase, which host Al_2O_3 -rich orthopyroxenes (up to 6% Al_2O_3) indicative of crystallization at great depth. Charnockitic microgabbros and diorites are particularly rich in incompatible elements. These characteristics were enhanced by magmatic flowage of the charnockitic parental magmas in the crust. Eight samples from the anorthositic to charnockitic suite and associated granites and pyroxenites define a Sm-Nd errorchron with an age of ~2.8 Ga, suggesting significant mantle magmatism and local crustal remobilisation in the Late Archean. Preliminary data obtained from zircons confirm these chronological results.

Effects of organic acids on interaction of actinides with microorganisms

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Actinides are highly toxic because they emit high-energy alpha-particles and have long half-lives. Plans to dispose of HLW and TRU wastes in geological disposal repositories have raised a number of concerns about polluting the environment through dissolution and subsequent mobilization of actinides; thus, long-term assessments of safety are required. TRU wastes contain cellulosic materials, scintillation fluids, waste oils, decontamination reagents, and chemical reagents. Among them, organic acids, such as citric acid, malic acid, and EDTA form stable complexes with multivalent actinides, enhancing their mobility by increasing their solubility. However, little is known of the interaction of actinides with microorganisms and organic acids. In this paper, we summarize our findings on the interactions of actinides with microorganism and organic acids.

Adsorption of Pu(IV)-, Th(IV)- and Eu(III)-desferrioxamine B (DFO) on bacteria of a Gram-negative bacterium *Pseudomonas fluorescens* or a Gram-positive bacterium *Bacillus subtilis* was studied. Adsorption of Pu(IV), Th(IV) and Eu(III) on *P. fluorescens* cells decreased in the order Eu(III) > Th(IV) > Pu(IV), which corresponds to the increasing the stability constant of the DFO complexes. These results indicate that Th(IV), Pu(IV) and Eu(III) dissociate from DFO by contact with cells, after which the metals ions are adsorbed.

Effect of Eu(III) on the degradation of malic acid by the bacterium *P. fluorescens* was studied. The chemical species of Eu(III) estimated by the thermodynamic data indicated that the degradation of malic acid was independent of $\text{Eu}(\text{Mal})_2^-$, and was hindered by the presence of EuMal^+ and free Eu^{3+} . The degradation was followed by the production of metabolites which were associated with Eu(III). One of the metabolites was analysed to be pyruvic acid.

A new geochemical index for evaluating crustal weathering and paleoclimate

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The present work introduces a new chemical weathering index that is derived from multivariate statistical analysis of a large weathering profile database (major oxide composition). Extracted latent variables from the database have been reformulated to a ternary "MFW diagram". The M and F values characterize mafic and felsic parent materials, respectively, while the W value identifies the degree of weathering of these materials. The degree of weathering represented by the W index is mathematically independent to the chemistry of the parent material. Two potential applications of the MFW diagram for the crustal recycling and the weathering processes will be discussed.

(1) Weathered materials and detritus delineate a weathering trend on the MFW diagram. Therefore, the composition of the destructed continental crust can be reconstructed simply by tracing the weathering trend backward to the unweathered domain. For example, weathering trends of the Archean and post-Archean sediments commonly extend backward to the domain of mafic and felsic source, respectively, which reflects the compositional evolution of the continental crust.

(2) Figure 1 compares W values of the recent soils developed in a various climate. The W index increases progressively as a climate becomes temperate and moist. Therefore, climates can be predicted by determining the W values of soils and paleosols, which aids to understand the Earth's surface condition and the recycling of continental crust.

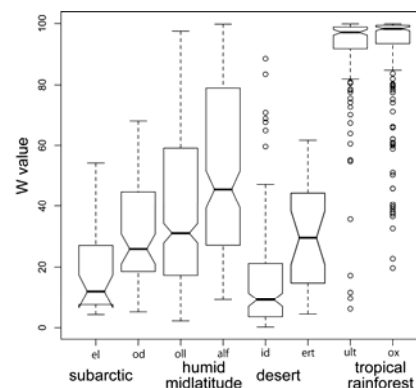


Figure 1: Boxplots of W values for various zonal soils.

Phase relations and compression of FeSi and FeNiSi Alloys: Implications for silicon content of the core

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The density of the core is about 2-5 weight % lower than the density of pure Fe at the core conditions, indicating the presence of low atomic weight components (such as H, C, O, Si, or S) [1]. Solar abundance suggests that Ni which is denser than Fe is expected to exist in the core. Si is a major candidate for the light element in both inner and outer cores because it is one of the most abundant elements in the Earth. Here, we report the phase relations and compression behaviors of Fe 3.4wt%Si alloy and Fe 9.8wt%Ni 4wt%Si alloys.

A double sided laser heated diamond anvil cell (DAC) with beveled diamond anvils was used for study of the phase relations and compression of the alloys. A sample foil was sandwiched in thin layers of NaCl, which was worked as a pressure-transmitting medium, and an internal pressure standard [2]. *In situ* X-ray diffraction experiments were carried out using the synchrotron X-ray at the BL10XU beam line, Spring-8. The results on Fe 3.4 wt% Si alloy revealed that fcc and hcp phases coexist up to 104 GPa, whereas the hcp phase is stable at higher pressures at least up to 3600 K at 242 GPa and to 2400 K at 257 GPa. EOS's for the Fe-9.8 wt% Ni-4.0 wt% Si and the Fe-3.4 wt% Si alloys were investigated at room temperature up to 374 GPa and 252 GPa, respectively. The compression curves are fitted to the third order Birch-Murnaghan EOS with the zero-pressure parameters: $K_0 = 167(36)$ GPa, and $K'_0 = 4.7(4)$ for hcp-Fe-9.8 wt% Ni-4.0 wt% Si and $K_0 = 196(20)$ GPa, and $K'_0 = 4.3(2)$ for Fe-3.4 wt% Si.

The present compression data on the Fe-9.8 wt% Ni-4.0 wt% Si and the Fe-3.4 wt% Si alloys combined with the previous data on FeNi and FeSi alloys [1, 3] and the core density of PREM revealed that the inner core likely possesses an hcp structure with a composition of Fe 82-85 wt. %, Ni 10 wt. %, and Si 5.4-7.7 wt. % if the inner core contains nickel about 10 wt % which is close to the chondritic abundance. The present silicon content of the core is greater than that estimated by previous workers.

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Magmatism in the Tsagaandelger, East Mongolian volcanic belt: Petrological and isotopic constraints on Mesozoic geodynamic setting

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The vast territory of Mongolia lies in the heart of the Central Asian Orogenic Belt, one of largest provinces of the Phanerozoic continental growth on Earth [1] We present new petrographic, geochemical and Sr-Nd isotopic analyses on Mesozoic igneous rocks emplaced in Central Mongolia. The Mesozoic igneous suites, those exposed in the Tsagaandelger area, pass upwards from alkaline series trachytic rocks and overlain by tuffaceous sediments. Those are intruded by calc alkaline leucocratic granites and covered by Late Mesozoic calc alkaline bimodal volcanic rocks consisting of basalts and rhyolite.

Alkaline series volcanic sequences were erupted in Early-Middle Triassic (241 Ma) and characterized by LILE and LREE enrichment and significant Nb-Ta depletion. Rocks have weakly enriched initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.705 to 0.706 and positive $\epsilon \text{Nd}(t)$ values (0.7 to 4).

The crystallization age of intrusive rocks is 231 Ma. The majority of samples is slightly peraluminous and can be classified as granite, including monzogranite, granodiorite and aplite. Granites are characterized by near-zero $\epsilon \text{Nd}(t)$ values (0.7 to 2) and tetrad effect in their REE distribution patterns.

Further Cretaceous volcanic sequences have lower contents of LILE and higher contents of HFS and REE, comparing with Triassic volcanic sequences. The Cretaceous volcanic rocks have the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.705 and 0.719 and near-zero $\epsilon \text{Nd}(t)$ values (-0.7 to 1.6).

Trace element geochemistry indicates that Mesozoic volcanic rocks from the studied area are arc related. The Triassic volcanic and plutonic rocks could be emplaced in active continental margin settings. Post collisional extensional regime could be started with Early Cretaceous volcanism. Moreover, the mass balance calculation suggests that the all Mesozoic volcanic and plutonic rocks were derived from sources composed of more than 80% juvenile mantle-derived component. Thus, our new data provide evidence for a significant production of juvenile crust, and hence growth of the continental crust, in the Phanerozoic.

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Investigating the chemical interactions between *Pseudomonas putida* and hematite using *in situ* flow-cell ATR-FTIR with a hematite-coated Ge crystal

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Hydrophobicity and electrostatic interactions are considered the primary mechanism of bacterial adhesion to mineral surfaces, as they can facilitate a closer approach between the bacteria and the surface so other adhesion interactions can occur. There is new evidence that, although favourable electrostatics contributes to bacterial adhesion, the formation of hydrogen bonds and inner-sphere complexes between a bacterium and a mineral could also play a role. In this work, *in situ* flow-cell ATR-FTIR using a hematite-coated Ge crystal was used to investigate the chemical interactions between *Pseudomonas putida* and hematite. The obtained FTIR spectra were compared to spectra from planktonic cells (not attached to the mineral surface). The symmetric stretching band of carboxylate anions ($\nu_{\text{sym}} \text{COO}^-$) for the *P. putida* attached to hematite shifted to higher frequencies when compared to the spectra obtained from unattached cells in both H₂O and D₂O suspensions, suggesting that carboxylate groups from macromolecules on the biofilm can be structurally coupled to the atoms on the hematite surface. The spectroscopic data of *P. putida* attached to hematite provided initial evidence that the surface chemistry of bacteria influences cell adhesion at mineral surfaces, and the adhesion of bacteria to solid surfaces may be mediated not only by electrostatic interactions or van der Waals forces, but also by a direct bonding of cell surface macromolecules at the mineral surface functional groups. The use of *in situ* flow cell experiments with a mineral-coated germanium crystal allowed a better description of the bacterial interactions with minerals in real time, as a further step to understand the fundamental mechanisms involved in the relationship between bacteria and mineral surfaces.

Evidence for anaerobic biodegradation of hydrocarbons in the subsurface environment

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Natural attenuation of hydrocarbons in impacted environments is potentially a strategy for site remediation. Biomarkers of anaerobic hydrocarbon degradation can be used to understand the anaerobic biodegradation processes in the subsurface and to evaluate a site for its potential to undergo natural attenuation. The biomarkers include unique metabolites of anaerobic degradation and gene analogues that encode enzymes catalyzing reactions in anaerobic degradation pathways. Groundwater samples from both within and outside the plume of a manufacturing gas plant impacted site were analyzed for the presence of a catabolic gene and metabolic intermediates of anaerobic hydrocarbons degradation. Genes encoding the alpha subunit of benzylsuccinate synthase (*bssA*) were detected in all water samples from within the plume while they were not detected in samples outside the plume. Benzylsuccinate synthase-like enzymes are involved in activation of a suite of hydrocarbons during anaerobic degradation processes, including alkanes, toluene, xylenes, naphthalene and 2-methylnaphthalene. PCR products were also obtained when primers specific for the *bssA* gene in toluene degrading denitrifying or sulfate-reducing bacteria were used suggesting the presence of a diverse community of anaerobic hydrocarbon-utilizing bacteria. GC-MS analysis of solvent extracts of groundwater samples was undertaken to identify the unique metabolic intermediates of anaerobic degradation of PAHs. Metabolites identified from samples from within the plume include 2-naphthoic acid (2-NA), tetrahydro-2-NA, hexahydro-2-NA and methylnaphthoic acid. The highest concentration of these metabolites was detected downstream of the source and within the plume; this was also characterized by low dissolved oxygen and negative oxidation-reduction potential. Collectively, the presence of *bssA* gene along with the specific metabolic intermediates of anaerobic degradation of PAHs within the contaminant plume while generally absent outside the plume, indicate that bacteria capable of anaerobic hydrocarbon degradation are present in the subsurface and are actively degrading the substrates. These data suggest the importance of anaerobic degradation processes *in situ*, at a site, which has been historically impacted with mixed hydrocarbon waste.

Oxide charge and electric-double layer control on phospholipid adsorption and self-assembly at oxide surfaces

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We have used bulk adsorption isotherms and atomic force microscopy to examine the interactions of cell membrane-forming phospholipids on oxide surfaces, at pH 7.2. Vesicle adsorption and bilayer self-assembly of dipalmitoyl-phosphocholine (DPPC) increases as oxide point of zero charge (PZC) increases, from quartz to rutile to corundum. The results are interpreted in terms of an interfacial model with contributions from electrostatic and van der Waals for adsorption. Incredibly, the effects of surface charge and diffuse layer counter-charge are observed even at distances as large as nanometers away from the surface, suggesting a “thickening” of the diffuse layer due to physical exclusion of solution from the vicinity of the oxide surface by the sheer bulk of the DPPC bilayer. The model is verified by changing ionic strength with NaCl and by adding Ca²⁺ to the solution, which affect diffuse layer thickness. Thus, crystal chemistry and interfacial solvation, which ultimately control PZC, and interfacial electrostatic and vdW forces control cell membrane-mineral interactions even at long distances. These results indicate the significance of the Stumm and Schindler legacy in modern biogeochemistry. Our study has implications for pre-biotic evolution of cell membranes, development of oxide-supported lipid bilayers for biosensors, and for making orthopedic implants more biocompatible.

Belemnite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ record of the Lusitanian Basin Pliensbachian carbonate series (Portugal)

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The hemipelagic series of the Pliensbachian-lowermost Toarcian section of Peniche (Portugal), comprising approximately 110m, shows a diverse set of geochemical occurrences of great importance for the palaeoceanographical interpretation of the referred time span. In the present study, after determination of sample alteration using geochemical proxies (Fe, Mg and Sr), $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ were determined in 109 belemnite rostra samples.

From the $\delta^{18}\text{O}$ record and the palaeotemperature calculations (following [1]), is possible to infer that the lowermost Pliensbachian is characterized by a noticeable cooling-salinity increase trend followed by a phase of warming-salinity decrease towards the upper Margaritatus Zone. Afterwards, a cooling tendency is observed until the middle Spinatum Zone. The uppermost Spinatum-extreme base of Polymorphum (Toarcian) Zones show an important warming phase, also observed in oxygen isotopic data from brachiopods [2].

Two striking features are associated to the $\delta^{13}\text{C}$ record. The first concerns the overall tendency of increasing $\delta^{13}\text{C}$ towards the upper Margaritatus Zone where several organic rich intervals are recorded. The second is the negative excursion that ends at the base of Polymorphum Zone.

Several of these geochemical events are also recognized in other European basins (e.g. [3, 4]). Taking in account the privileged palaeogeographic position of the Lusitanian Basin, between the Atlantic and Tethyan sectors, the present study has important implications in future environmental interpretations.

The present study is a contribution to Project PDCTE/CTA/44907/2002.

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The sources of gold and associated elements in Carlin-type deposits, Northern Nevada, USA: Litho geochemistry and mineral chemistry constraints

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Carlin-type deposits in northern Nevada, which provide ~9% of world gold production, are hosted mainly in hydrothermally altered Paleozoic impure carbonate rocks as well as in various types of Jurassic and Eocene intrusive rocks. The main auriferous event took place in the Eocene during the onset of the Basin and Range extension. Gold occurs in arsenian pyrite and is commonly associated with other elements such as Cu, Sb, Ni, Se, Hg, Tl, Ti, Zn, Ag, Co, Pb, and W. Despite the large gold endowment and more than 40 years of research, very little is known about the source of metals and fluids associated with Carlin-type gold deposits.

Our extensive litho geochemistry and mineral chemistry investigation at the Goldstrike Property, which comprises the largest Carlin-type deposits, suggests that some of the sedimentary and intrusive rocks, and probably magmatic fluids exsolved from Eocene magmas, may have been sources for gold and some of the ore-related elements.

The Jurassic phlogopite lamprophyre dikes are interpreted to be one of the possible local sources of gold as their freshest samples have gold contents up to 40 ppb and comprise magmatic As-poor, Co-rich pyrite containing up to 100 ppm Au. Gold was neither detected in igneous pyrite in any of the other intrusive rocks, nor in pre-ore pyrite in the sedimentary rocks. Intriguingly, the magmatic pyrite in the Eocene porphyritic dikes is very poor in elements associated with the Carlin-ore when compared with data obtained from other units. These data, and the fact that these Eocene dikes are temporally and spatially associated with gold mineralization and emplaced at shallow levels, favor the hypothesis that gold and some elements associated with Carlin-ore were scavenged from the magma by magmatic fluids that exsolved during its early stage of crystallization. This process would have prevented the incorporation of these ore-related elements in the magmatic sulfides. Furthermore, the sedimentary units, in particular those enriched in carbonic matter, are probably the most important local sources of Mo, Zn, Ni and Se and to a lesser extent of As, Cu, Hg and Sb, as their unaltered samples are commonly enriched in these elements.

EarthKin: An online geochemical kinetics database

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EarthKin is an online database designed as a repository for geochemical kinetics data. *EarthKin* is the only database of environmental kinetics that is currently online. The database was synthesized from the literature by personnel at the Center for Environmental Kinetics Analysis (CEKA) at Penn State University. The database is currently accessed and facilitated within *Chem_xSeer* (<http://chemxseer.ist.psu.edu/>), an online cyberinfrastructure that enables the use of chemical data online.

We envision that *EarthKin* will provide permanent global access to environmental kinetics data. *Chem_xSeer* will provide tools and utilities to invite researchers to both add and compare new this data to existing data. Currently, *EarthKin* contains primarily mineral dissolution kinetics data that has been compiled from papers in the literature, although we hope to add data for the rate of heterogeneous mineral-water reactions including cation exchange, precipitation, and bioreaction. We hope to continue to compile legacy data for inclusion in *EarthKin*, but we also hope to encourage scientists who are not currently affiliated with *EarthKin* to add new data to the database.

Observations of some post-sourcing alteration factors on the metal signature of crude oils

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The influence of post-sourcing alteration effects on the metal composition of petroleum is presented from a number of case studies. Metals in oils from North Sea migration sequences on the Central Graben and Tampen Spur will be used to illustrate the influence of migration on metals. The effects of maturation, asphaltene precipitation, phase-controlled fractionation and biodegradation will be illustrated using case studies done on oils from the North Sea, China and the USA.

For example, metal data for the Tampen Spur migration sequence [1] is shown in Table 1. Maturity, rather than migration processes controls the metal contents of the Central Graben oils. The V/(V+Ni) ratio is a maturation and migration independent source facies indicator.

| Sample | API | $\frac{V}{V+Ni}$ | V | Ni | Co | Zn | $\frac{T_s}{T_m}$ |
|--------|------|------------------|-------|-------|----|------|-------------------|
| Oil 1 | 40.7 | 0.889 | 820 | 102 | 2 | 110 | 5.0 |
| Oil 2 | 38.4 | 0.918 | 8700 | 780 | 1 | 160 | 3.1 |
| Oil 3a | | 0.888 | 15790 | 1993 | 4 | 547 | 2.8 |
| Oil 3b | 38.2 | 0.911 | 8876 | 867 | 4 | 294 | 2.8 |
| Oil 3c | 37.4 | 0.909 | 13535 | 1350 | 6 | 407 | 2.7 |
| Oil 4 | 32.5 | 0.903 | 68180 | 7333 | 9 | 572 | 1.4 |
| Oil 5 | 33.3 | 0.898 | 88970 | 10150 | 15 | 2930 | 1.4 |

Table 1: Metals in central Graben oils (ng/g oil).

Examples will be given of metals such as Zn, Pb and Au introduced to source rocks and their oils due to incorporation of minerals from nearby mineralized zones during formation of the source rock. Indications of possible incorporation of Fe into oils due to the action of Fe (III) reducing bacteria and of Co due to methanogenic bacteria will be presented.

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Characterization of secondary mineral formation on olivine by surface sensitive techniques

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The world faces a huge challenge to decrease carbon dioxide emission while maintaining reasonable growth. With a still increasing use of fossil fuels, a need is arising to develop methods for removing CO₂. A promising way to meet this challenge is to sequestering CO₂ as solid carbonate minerals.

The silicate mineral olivine, (Mg,Fe)₂SiO₄ reacts exothermally with carbon dioxide and forms other minerals, including carbonates. Unfortunately, the reaction rates are slow at standard temperature and atmospheric CO₂ pressure because olivine dissolution is slow, which makes mineral carbonation economically unfavourable. Changing the conditions, including pH, or using a catalyst can increase the reaction rate considerably.

An atomic force microscopy (AFM) study of a freshly fractured olivine (Fo₉₀) surface showed almost instantaneous mineral formation after rinsing the samples with Milli-Q water. After an hour, features grew, changed shape and distribution. Reaction favoured some sites on the fresh surface over others, indicating non-homogeneity either in composition or in crystal defects. Dissolution and a considerable increase in mineral precipitation were observed when olivine was heated for 4 hours at 160 °C in Milli-Q water, in an autoclave reactor. With higher CO₂ (P_{CO₂}=25 bars) and increased reaction time (15 hours), the green olivine surface turned red. X-ray powder diffraction (XRPD) could not identify the red precipitate, suggesting: 1) an amorphous phase, 2) too little material, or 3) the XRPD pattern of the red material was masked by an olivine peak. X-ray photoelectron spectroscopy (XPS) of the red precipitate showed a high proportion of iron and at least one additional oxygen binding environment. By comparing the XPS spectra for the red precipitate with iron oxide standards, the material was interpreted to be hematite (Fe₂O₃). New experiments to investigate the surface changes during exposure to higher pH solutions are underway.

Enzymatic and abiotic hydrolysis of glucose-1-phosphate adsorbed on goethite: Kinetics and molecular mechanisms

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Hydrolysis is usually a required step in order to make phosphorus in organophosphates bioavailable as only orthophosphate or small organophosphates may cross cell membranes. This process is catalyzed by extracellular enzymes present in soil solutions, or by an abiotic process at mineral surfaces. In this study we have investigated the enzymatic and abiotic hydrolysis of glucose-1-phosphate adsorbed at the water-goethite interface. Glucose-1-phosphate is produced in glycogenolysis and it has also been used in soil bioassays as a model substrate where the bioavailability was shown to be on the same order as orthophosphate.

To characterize the kinetics and molecular mechanisms of the hydrolysis of glucose-1-phosphate adsorbed on goethite surfaces in presence and absence of an enzyme (acid phosphatase) we have used a combination of wet-chemical and spectroscopic methods. Concentrations of solutions species were determined by means of ion chromatography while the surface reactions were monitored by infrared spectroscopy using the ATR sampling technique.

The spectroscopic results show that glucose-1-phosphate forms two surface complexes on goethite in the pH range 3 – 10. Below pH 7 these complexes are stable with respect to hydrolysis whereas at higher pH values a small extent of hydrolysis is detected. Maximum rate of abiotic hydrolysis is between pH 9-10 where ca. 4% of the adsorbed ligand is hydrolyzed after 48h. In presence of phosphatase the hydrolysis of adsorbed glucose-1-phosphate increases dramatically; at pH 4.8 17% is hydrolyzed after 26h. IR data indicate that hydrolysis is related to the co-adsorption of enzyme at the glucose-1-phosphate covered goethite particles. Furthermore, the amount of glucose-1-phosphate adsorbed has a profound effect on enzyme adsorption and thus the enzymatic hydrolysis. This will be further discussed.

The use of Low Earth Orbit to select for extremophilic cyanobacteria

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Cryptoendolithic cyanobacteria can survive long periods of desiccation, low temperature, and UV radiation; which are all prerequisites for life in space and on Mars. Although several extremophilic cyanobacteria have been exposed to space conditions, this is the first communication that uses LEO to select for extremophilic cyanobacteria from a natural, non-extreme, cryptoendolithic environment.

A cryptoendolithic community from cliffs in Beer, Devon, UK was exposed to LEO. 16S rDNA analysis demonstrated that the cyanobacteria community consisted of the orders Pleurocapsales, Oscillatoriales, and Chroococcales. The rocks were sent into LEO for 10 days as part of the ESA funded BIOPAN VI mission and returned for analysis.

An extremophilic cyanobacterium, which was coccid in nature and phylogenetically identified as a member of the order Chroococcales, survived 10 d in LEO. Ground based experiments showed that the isolate was also able to survive 28 d of exposure to desiccation and Mars simulated conditions, 10 d of exposure to vacuum, and ionization radiation (3 KGy). The isolate was unable to survive exposure to UV radiation. Additional cyanobacteria were isolated after the ground based experiments but none of these isolates survived exposure to LEO.

Little is known about the microbial requirements for survival in space. Extremophilic microbes isolated on Earth are not necessarily capable of surviving in this adverse environment. Consequently, the use of LEO as a selection factor, as demonstrated in this communication, is an ideal approach for isolating extremophilic microbes that can be used to study the physiological requirements for life in space.

Linking microbial community structure to groundwater arsenic concentrations in Pannonian basin wells

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The groundwaters within the Pannonian basin are known to have As concentrations that exceed the 10 ppb WHO provisional guide value. The mechanisms that govern As release, however, are unknown but believed to be microbially mediated. Microorganisms are capable of performing a wide variety of biogeochemical transformations that can influence the levels of As and other geogenic chemicals, such as S, Fe, and Mn. To date, it is not known which groups of microorganisms inhabit aquifer systems within the Pannonian Basin and their role, if any in geogenic chemical release mechanisms. In order to elucidate the role microbes play in groundwater geochemistry in this region, we collected water from artesian, pumped, and open dug groundwater wells in western Romania and eastern Hungary. The collected groundwaters ranged from mildly reducing to strongly reducing, with typical As concentrations between 1 and 200 ppb. We used a combination of 16S rRNA gene sequence analysis and terminal restriction fragment polymorphisms to investigate the communities in these systems. Our results revealed several types of known and unknown bacterial genera, capable of many types of transformations that can affect the cycling of As and other geogenic chemicals. The microbial communities present in groundwater wells in the Pannonian basin and their role in geogenic chemical cycling will be discussed.

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Arsenite sequestration by Fe(II)-containing minerals after microbial dissimilatory reduction of arsenic-sorbed lepidocrocite

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EXAFS and XANES were used in combination with HRTEM, XRD, and Mössbauer spectroscopy to obtain detailed information on arsenic and iron speciation in the products of anaerobic reduction of pure and As(V)- or As(III)-adsorbed lepidocrocite by *S. putrefaciens* ATCC 12099. We found that this strain is capable of using both Fe(III) in lepidocrocite and As(V) in solution or adsorbed on lepidocrocite surfaces as electron acceptors. Bioreduction of pure and As(III)-sorbed lepidocrocite resulted in the formation of hydroxycarbonate green rust 1 [GR1(CO₃)], prior to formation of ferrous-carbonate hydroxide (FCH). However, the presence of As(III) slows down this transformation, leading to the co-occurrence of both phases. As(III) was then found to be adsorbed on the surfaces of GR1(CO₃) and FCH. Bioreduction of As(V)-bearing lepidocrocite led directly to the formation of FCH in association with nanoparticles of a minor As-rich Fe(OH)₂ phase, with no evidence for green rust formation. As(V) was fully converted to As(III) and dominantly sorbed at the surface of the Fe(OH)₂ nanoparticles as oligomers binding to the edges of Fe(OH)₆ octahedra in the octahedral layers of Fe(OH)₂. These multinuclear As(III) surface complexes are characterized by As-As pairs at 3.32 ± 0.02 Å and by As-Fe pairs at 3.50 ± 0.02 Å and represent a new form of As(III) surface complexes. Chemical analyses show that the majority of As(III) is associated with iron-bearing hydroxycarbonate or hydroxide solids, reinforcing the idea that, at least under some circumstances, bacterial reduction can promote As(III) sequestration instead of mobilizing it into solution.

Reconciling the contradicting results from computational and experimental studies of high-pressure minerals

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Recently, the great success of *ab initio* simulation has contributed to improve our understanding of the inner Earth's dynamics. In contrast, high-P experiments have also provided valuable data. The combination of different scientific perspectives is necessary for the development of a consistent model of the Earth's mantle and core. However, some results from *ab initio* computations contradict those from high-P experiments. In order to reconcile these issues, we have performed both DFT computations and synchrotron high-P experiments. VASP code and diamond anvil cell were used for *ab initio* computations and high-P experiments, respectively. In this talk, three issues (magnesium-aluminium oxide, carbonate, and iron carbide) will be presented. In the case of magnesium-aluminium oxide ($MgAl_2O_4$), previous computational study [1] could not explain the pressure-induced transition sequence observed in high-P experiments. Our experimental [2] and computational [3] studies showed that previous computational study had a significant uncertainty for comparing energetics of different structures, because of a lack of the relaxation of atoms. In the case of carbonate ($CaCO_3$), a new mineral predicted by *ab initio* simulations [4] could be synthesized by diamond anvil cell experiments [5]. The new high-P phase of carbonate has a four-fold coordination of carbon cations. In the case of iron carbide (Fe_3C), the magnetic transition pressure is inconsistent (5~70 GPa) among previous experimental studies. In contrast, *ab initio* simulations predicted that the magnetic transition occurs at ~60 GPa [6]. Our results from both high-P experiments and *ab initio* simulations showed the transition pressure was ~55 GPa. This indicated that previous experiments have a large uncertainty for the detection of the change in magnetic properties of iron carbide.

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A provenance study of marbles from the Roman town of Thamusida (Mauretania Tingitana, northern Morocco)

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A combined mineralogical and geochemical approach is being used to determine the provenance of the white and coloured marbles found in the archaeological site of *Thamusida* in Mauretania Tingitana Roman province, northern Morocco. Of particular interest is to assess the exploitation and use of local raw material that mostly consists of limestone and metamorphic marble of the coastal Paleozoic basement. 75 samples from ancient and modern quarries, covering as many different lithotypes as possible, were compared with 26 fragments from archaeological artefacts. Both sample sets were submitted to petrographic and mineralogical studies, using OM, SEM, and XRD. The geochemical analyses include major and trace elements and stable C and O isotope compositions.

The archaeological samples made of crinoidal grainstone ($\delta^{13}C$: 0.4 and 0.7‰, $\delta^{18}O$: -5.3 and -3.9‰ VPDB) and the one made of packstone ($\delta^{13}C$: 1.8 and $\delta^{18}O$: -7.3‰) fall within the ranges ($\delta^{13}C$: 0.2 to 2.2‰, $\delta^{18}O$: -3.1 to -5.8‰ and $\delta^{13}C$: 0.2 to 2.4‰ to $\delta^{18}O$: -5.1 to -10.8‰) defined for the quarries located in the Tiflet-Sehoul zone (SE Rabat). The local white marbles have an isotopic composition ($\delta^{13}C$: -2.0 to 2.4‰, $\delta^{18}O$: -15.8 to -7.8‰, n= 28) significantly different to that of the white marble artefacts ($\delta^{13}C$: -0.9 to 3.5‰, $\delta^{18}O$: -8.1 to -1.6‰, n= 21). This data indicate that Moroccan material can be excluded as source of the studied white marble artefacts. The comparison with published database on Mediterranean marbles allowed identifying some other provenances, such as Carrara marble for a 'Togato' statue ($\delta^{13}C$: 2.2‰ and $\delta^{18}O$: -1.7‰). The results of this work give for the very first time a detailed characterization of local stone material from the area of *Thamusida*. The stable isotope data point clearly to the provenance of some artefacts, particularly those made from coloured limestones.

Geochemical variation of fresh quenched glass in axial MORB along 15-18°S, Central Indian Ridge

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The Rodrigues Ridge bifurcating from the Reunion hotspot track meets the Central Indian Ridge (CIR) at 19°S, and provides the best opportunity to understand ridge-hot spot interaction. The CIR MORBs have enrichment in incompatible elements increasing gradually northward along 18-21°S [1]. However, it is controversial that the increase of enrichments results from either an input of the plume materials channeled from the Reunion hot spot beneath the lithosphere and dammed by the Marie Celeste Fracture Zone (MCFZ) [1] or metasomatic process in the upper mantle such as recycling of ancient alkali basalts of subducted oceanic island [2]. In order to clarify the above issue, it is important to reveal distribution of the E-MORBs along the CIR over the MCRZ. We dredged the axial MORBs along 15-18°S during KH06-04 cruise and measured major and trace element compositions of the recovered fresh quenched glasses. Our result indicates that E-MORBs having high La/Sm, Ba/Nb and Nb/Zr ratios are distributed up to 15°S in CIR, and that the glasses with strongest enrichment signature are distributed near the MCRZ. The plume materials dispersed along the CIR might be lately overprinted by metasomatism related to the MCFZ.

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S and O functional analysis of aqueously altered carbonaceous chondrites IOM

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CI1, CM2, CR2 and ungrouped C2 carbonaceous chondrites contain a few percent of insoluble organic matter (IOM) which could provide clues on the organic chemistry of nebular and/or protostellar environments. These chondrites also have experienced complex hydrothermal processes on parent bodies [1-3]. A major issue is the understanding of IOM compositional and structural changes due to hydrothermalism. Chemical variability has been reported among various IOMs, and so far interpreted as the consequence of oxidation processes [4; 5]. The primordial diversity of organic precursors could be also involved.

11 IOMs extracted from CI1: Ivuna, Orgueil, Alais; CM2: Murchison, Cold Bokkeveld, QUE99355, QUE97990, Mighei, Murray; CR2: Renazzo; and C2 ungrouped: Tagish Lake were measured with μ -IR and S K-edge μ -XANES spectroscopy (in Grenoble, at LPG and ESRF, resp.).

CI1 and C2 IOMs can be systematically distinguished regarding their oxidised groups. Indeed, CI1 IOMs show sulfonyl and carboxyl features on XANES and IR spectra. CI1 aliphatic enrichment toward CM is consistent with previous IR and NMR studies [5; 6]. Each in their group, Cold Bokkeveld (most altered CM) and Alais (least altered CI1 [7]) have peculiar IOMs: one exhibits abnormally oxidised sulfur and the other seems to be richer in aliphatics. If there are not precursor effects, the crescent IOM oxidation state seems to be driven by the increasing alteration degree.

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Intra- and inter- speleothem variability of bacterial communities in Kartchner Caverns

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Kartchner Caverns is a wet living carbonate cave located in the Whetstone Mountains in Benson, Arizona, USA. It was added to the National Science Foundation's Microbial Observatories (MO) in 2006. This cavern is considered one of the top ten caves in the world in terms of its mineral and speleothem diversity. It contains minerals from six different chemical classes; carbonates, sulfates, oxides, nitrates, silicates and phosphates [1]. Kartchner Caverns is an extremely oligotrophic environment with high CO₂ and high humidity. One goal of the MO is to determine the heterogeneity of bacterial communities and mineral composition of speleothems in the cave. This study examined nine different speleothems and one flowstone that were in an area of 10 m (length) x 2 m (width) located in a single room of the cave. The objective was to explore both, intra- (on the same speleothem) and inter- (different speleothems) speleothem variability in bacterial community structure and mineral composition. Bacterial community fingerprints were generated from each speleothem by denaturing gradient gel electrophoresis (DGGE) analysis of 16S rRNA gene fragments. An elemental profile of each speleothem was also performed using inductively coupled plasma mass spectrometry (ICP-MS) analysis. The intra-speleothem analysis revealed that the community profiles from the same formation are more similar than the ones from different speleothems. For the inter-speleothem analysis, four clusters were observed which were primarily associated with the spatial location of the formations. Elemental analysis revealed differences in the trace mineral content of the ten formations. These are being explored for correlations with the DGGE bacterial community profiles. In a further study, pyrosequencing of the 16S rRNA gene fragment from the bacterial community DNA of the ten formations will be initiated Summer 2009.

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¹²⁹I and Sr isotopes as tracers of large-scale fluid migration in the northern Appalachian Basin (USA)

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Results from previous studies of ore deposits, fluid inclusions, clay mineral assemblages, and hydrologic modelling suggest that brines and hydrocarbons have migrated long distances across the Appalachian basin, driven by topographic gradients and tectonic forces. This pilot study uses iodine and strontium isotopes of basinal fluids as tracers of brine migration in the northern Appalachian basin (W. NY and N.W. PA).

Ten brine samples were collected from oil and gas wells producing from Mississippian, Devonian, and Silurian age formations and analyzed for ¹²⁹I/I, ⁸⁷Sr/⁸⁶Sr, stable isotopes (O, H, and C), and elemental composition. Measured ¹²⁹I/I values (28-1890X10⁻¹⁵) are 5 to 9 orders of magnitude greater than expected cosmogenic values (10⁻¹⁹ to 10⁻²¹), given the depositional age (>350 Ma) of the source organic matter. Fissionogenic ¹²⁹I/I values (50-100X10⁻¹⁵) in Devonian shales were estimated from published ²³⁸U (spontaneous fission to ¹²⁹I) data and can account for only 7 of the high ¹²⁹I/I values. Large ²³⁸U deposits in S.E. PA represent a regional fissionogenic iodine source (calculated ¹²⁹I/I up to 17,000X10⁻¹⁵) that may have been mobilized during the Alleghanian orogeny (~315 Ma). Strontium isotope results show a mixing trend between a radiogenic (0.7210) end-member (consistent with exchangeable ⁸⁷Sr/⁸⁶Sr on smectite-illite clay assemblages), with a low ⁸⁷Sr/⁸⁶Sr (0.7100) end-member (within the range of Paleozoic marine carbonates in the Appalachian Basin). K⁺/Cl⁻ ratios, less than the evaporated seawater trend, have a weak correlation with radiogenic Sr values and may provide evidence for punctuated clay diagenesis (illitization) by high temperature fluids expelled basinward, likely during orogenic events.

Simulated 21st century's increase in oceanic suboxia by CO₂-enhanced biotic carbon export

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Using a model of global climate, ocean circulation and biogeochemical cycling, experimental findings of a pCO₂-sensitive increase in biotic carbon-to-nitrogen (C:N) drawdown and of pCO₂-sensitive changes in nitrogen fixation and diazotroph composition are extrapolated to the global ocean. For a simulation run from the onset of the industrial revolution until A.D. 2100 under a "business-as-usual" scenario for anthropogenic CO₂ emissions, the model predicts a negative feedback on atmospheric CO₂ levels that represents a small alteration of the anthropogenic perturbation of the carbon cycle. Changes in simulated nitrogen fixation remain relatively small on decadal and longer timescales because of negative feedbacks mediated by inorganic nutrient inventories. Still, the model results reveal a dramatic 50% increase in the suboxic water volume by the end of this century in response to the respiration of excess organic carbon formed at higher CO₂ levels. This is a significant expansion of the marine "dead zones" with severe implications not only for all higher life forms, but also for oxygen-sensitive nutrient recycling and hence for oceanic nutrient inventories.

Geochemical proxies for paleoprecipitation and drought from Lake Tahoe cores: California and Nevada, USA

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Sediment cores from >400 m water depth in Lake Tahoe reveal a long-term history of suspension fallout interspersed with turbidites generated by severe storms and associated hyperpycnal currents over the last 7000 years. Relative to fine-grained 'background' sediments, the majority of Tahoe turbidites exhibit coincident trends of increased mean grain size, increased magnetic susceptibility, decreased TOC, higher $\delta^{13}\text{C}_{\text{org}}$ and variable C/N. The shift in $\delta^{13}\text{C}_{\text{org}}$ toward higher values within turbidites is interpreted to record the input of soil organic matter within runoff from the watershed triggered by high-intensity storms.

Tahoe turbidites tend to occur in clusters, separated by intervals of fine-grained mud, suggesting a changing frequency of severe storms and potentially long-term paleoprecipitation levels. To test our hypothesis that turbidite frequency records paleoprecipitation levels, we compared the timing of our correlated Tahoe sediment record with published paleoclimatic proxies for 1) elsewhere in the Tahoe basin, 2) lakes in the western Great Basin whose level is directly related to runoff from the Sierra Nevada, and 3) the San Francisco bay estuary. The reasonable degree of temporal overlap suggests that apparent trends in severe storm frequency recorded by clusters of turbidites provides a measure of millennial-scale regional paleoprecipitation and drought. We recognize an extended phase of dryness and a near absence of major storms between ~3000 and ~700 cal yr B.P. in the Tahoe watershed, partly coincident with the Medieval Climate Anomaly and two mega-droughts previously recognized in other climate records.

Stalagmite records of Pleistocene and Holocene climate from the Sierra Nevada, California

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Stalagmites from caves developed on the western slope of the central Sierra Nevada, California (38°N), exhibit abrupt isotopic and elemental changes over the past 75kyr that track changes in climate in the North Atlantic region, suggesting an atmospheric linkage between the two regions. Abrupt shifts to more negative $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, lower trace element concentrations, and less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ in a $^{230}\text{Th}/\text{U}$ -calibrated stalagmite (Moaning Cave) are coeval to within the dating uncertainty with the Older and Younger Dryas and Inter-Allerød Cold Period, indicating shifts to wetter conditions coincident with the onset of Northern Hemisphere cool periods.

Conversely, Northern Hemisphere warm periods (Bølling, early and late Allerød) are represented by increases in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, elevated trace element concentrations, and more radiogenic, host rock dominated $^{87}\text{Sr}/^{86}\text{Sr}$ values suggesting shifts to drier conditions above Moaning Cave. Preliminary data from a stalagmite, collected from a cave developed within the same Sierran marble pod, documents decreased $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ during the transition out of interstadial 20 at $\sim 69\text{ka}$, indicating wetter conditions during earlier cool periods. These results suggest that changes in water-soil-rock interactions, driven by past changes in precipitation, occurred in the Sierra Nevada in synch with Northern Hemisphere warmings and coolings.

Raman spectroscopic identification of phthalic and mellitic acids in mineral matrices

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The possibility of life on Mars has fascinated mankind for centuries. The 1976 Viking missions failed to detect organic molecules on the Martian surface, even those expected from meteoritic bombardment. Since then, it is believed that the Martian regolith is highly oxidative and converts all organic molecules to metastable intermediates, which might be embedded in soils and rocks. Several types of organic compounds are known to have come to Mars via meteorites. Naphthalene, phenanthrene and anthracene all convert to phthalic acid in the generic oxidation process, and higher polycyclic aromatic hydrocarbons and kerogen transform into benzenecarboxylic acid products (e.g., mellitic acid) during oxidation [1].

In this study, we compare 785 nm and 514 nm excitation wavelengths of Raman spectroscopy to test this nondestructive method as a means to determine the presence of these two carboxylic acids (phthalic and mellitic acids) in experimentally prepared mineral matrices. This approach was first tested using beta-carotene [2] and usnic acid [3]. Samples consisting of carboxylic acid mixed one by one with powdered minerals (gypsum, epsomite and halite) were studied. Various concentrations of carboxylic acids (25, 10, 5, 1wt%) in the mineral matrices were studied to determine the detection limits of Raman spectroscopy for the detection of these biomarkers. Carboxylic acids mixed with mineral powders were then covered by a UV-transparent crystal of the same minerals, thereby creating a type of artificial inclusion. If a similar concentration of these acids exists in Martian samples, then Raman spectroscopy will be able to identify it.

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Molecular hydrogen and the process of thermochemical sulfate reduction

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The process of thermochemical sulfate reduction (TSR) refers to the abiotic conversion of sulfate sulfur to a more reduced sulfur species, most often hydrogen sulfide. It is well documented for a variety of natural environments. The process itself involves the oxidation of a reduced compound. Despite the knowledge of a number of possible redox partners for sulfate that might be relevant under natural conditions, all experimental and modelling studies during the past years have been directed towards the direct interaction of reduced organic carbon compounds and sulfate. The experimental approaches under relatively inert conditions – in sealed gold capsules or in flexible Dickson-type gold-titanium hydrothermal cells – have resulted in interesting new data on the kinetics of the overall reaction (e.g. [1]), that are in broad agreement with data from modelling studies. But the detailed understanding of the reaction itself is not adequate.

Studies reporting a more comprehensive analysis of gases evolved during the reaction document significant amounts of molecular hydrogen as byproduct (e.g. [2]). Based on existing thermodynamic data the direct reduction of sulfate by hydrogen is possible at natural temperatures.

In addition to this finding of hydrogen production during TSR under experimental conditions, a puzzling discrepancy of reaction rate in experiments with differing water/rock ratios calls for alternative explanation avenues. For example [1] reported a variation in H₂S production of more than two orders of magnitude for water/rock ratios of 0 to 20. And “dry” experiments focussing on the reaction between e.g. methane and solid sulfate at elevated temperatures resulted in high H₂S production rates.

Therefore this study investigates the possible role of molecular hydrogen as direct reduction agent for sulfate sulfur in the process of TSR – using both experiments with sealed gold capsules and flexible Dickson-type gold-titanium cells. In all experiments a significant production of molecular hydrogen was documented. This is true for the sealed gold capsules – even after prolonged acid-cleaning of the inner gold surface to remove possible traces of metal contaminants – and for the gold-titanium cells.

[1] Zhang *et al.* (2008) *Org. Geochem.* **39**, 308-328. [2] Zhang *et al.* (2007) *Org. Geochem.* **38**, 897-910.

Solar system formation hypothesis: Why the chemical compositions of the planets are so different?

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The current interpretation of the data on the interplanetary-dust isotopic ratios is ambiguous. Planet-formation hypothesis should include a simplest conceivable evolution pattern, which is rather possible to be multiply repeated in the Universe and is capable of explaining the principal features of the Solar System (SS) current state. We subdivide the SS bodies into the physically formed objects (PFO) located in the SS cold region (from the outside to the today Main Asteroid Belt) and chemically formed objects (CFO) located in the SS hot region. After the Supernova explosion, nebula expanded quickly and cooled steadily; H₂ and other two-atom molecules and hydride radicals formed. With time, nebula transformed to a flat thin disk composed of concentric diffusely-bounded rings; the more peripheral they were, the lighter molecules they tended to contain. PFO formation started, when the nebula began to collapse after its outer H₂ and He rings cooled to the H₂ condensation temperature; H₂ droplets absorbed light Li, Be, B, LiH, and BeH atoms and molecules, which formed the agglomerate cores and increased their size competing with each others for the mass and gravitational attraction. Heavy atoms and hydrides remained in that nebula section in which the temperature was too high for their physical agglomeration and in which their concentration was too low for chemical reactions to proceed. As the nebular-disc compressed, CFO formation started: combination reactions in the diffusive regions of the neighboring disc rings, heat evolution, and local concentration of matter accelerated exponentially and local giant compressible vortexes arouse. Within them, hot cores of the present sky objects localized. The reaction heat was capable of melting the cores. The pressure depletion in the vicinities of the vortexes and the gravitational attraction of the last stimulated flows of light cold vaporous and gaseous substances and the asteroid-like agglomerates from the outer space and also of asteroid-like agglomerates of not so light substances from the intermediate regions of the space to the hot cores within the vortexes. The flows precipitated over the hot core surfaces of the CFO and cooled them. The sandwiches obtained as a result of this precipitation became steadily the young terrestrial planets and their satellites.

Evolution of the hydrochemical system at Horonobe, Japan: An indication from rock matrix porewater chemistry

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The investigation of the geological environment within a suite of sedimentary formations is currently ongoing at the site of JAEA's Horonobe Underground Research Laboratory in northern Hokkaido, Japan. The main aim is to establish relevant techniques for future repository site characterisations in Japan. One facet of this is one of the few examples worldwide, and the first use in Japan, of rock matrix porewater data, in conjunction with groundwater data, as part of the evaluation of the palaeohydrogeological evolution of the Horonobe area.

More than 100 porewaters have been extracted from cores sampled from the marine sequences of the late Miocene to Pliocene Wakkanai and Koetoi Formations, consisting predominantly of siliceous and diatomaceous mudstones respectively. General trends, *eg* in Cl concentration with depth, indicated by all data, from both the porewater and groundwater datasets, are strikingly consistent. The data indicate the presence of a shallow zone of rapid change in hydrochemistry, followed by more stable conditions below 200–300 mbgl. The deep porewaters are more saline than shallow waters, but are still diluted (Cl = 2,000–15,000 mg/l) and enriched in ¹⁸O ($\delta^{18}\text{O} = 0\text{--}4\text{ ‰}$) compared to seawater. Although the Horonobe area was not directly glaciated, it is likely that permafrost was present discontinuously during the Last Glacial Maximum and later during the Kenbuchi Stadial (the local equivalent of the Older Dryas) of approximately 11.8 to 12.4 ka BP. The fact that no cold climate and glacial depletion signature is obvious in the porewaters suggests either relatively rapid flushing of the hydrochemical system to remove any evidence of the cold climate or complete sealing of the system by the permafrost against the cold climate signature.

A new analysis of the porewater stable isotope data suggests that the cold climate signature has been effectively removed by mixing with later groundwaters. Tests of this new interpretation against major element data and the M3 mixing model will be presented here.

First principles investigation of the FeOOH-polymorphs under pressure

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Iron-oxyhydroxides (FeOOH) play an important role in nature and technology: they find application in water treatment (e.g. binding heavy metals and arsenic complexes), as inorganic pigments, and in magnetic recording. The high pressure behavior of water containing minerals is fundamental for understanding processes in the Earth's crust and upper mantle.

Using density functional theory (DFT), we investigate the stability, structural, magnetic, and electronic properties of the FeOOH-polymorphs (α -, β -, γ -, and *hp*(ϵ)-FeOOH) under hydrostatic pressure. At ambient conditions goethite (α) is the lowest energy phase consistent with recent calorimetric measurements [1]. Around 9 GPa we predict a transition to the *hp*(ϵ)-phase. Indications for such a phase transition have recently been obtained using x-ray diffraction measurements [2]. This structural transformation is accompanied by a spin-crossover takes place at a much lower pressure than other currently discussed iron-bearing minerals. While the ground-state Fe³⁺-ions are coupled antiferromagnetically, at higher pressure a transition to a ferromagnetic alignment occurs for *hp*(ϵ)-FeOOH within the generalized gradient approximation (GGA). Concerning the electronic properties, including an on-site Coulomb repulsion parameter (LDA/GGA+U method [3]) improves the size of the band gaps at zero pressure substantially.

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Evolution of volcanic aerosol over the North Atlantic Ocean

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In the North Atlantic region volcanic exhalation from Iceland can be expected to significantly contribute to the natural SO₄ budget as sulfur gases typically comprise a large fraction of volcanic gas emissions, even at the quiescent stage. In addition, strong winds can generate dust storms over Arctic deserts, and dust plumes may be transported over great distances impacting on air quality in the British Isles and continental Europe [1]. Here we report real-time observations using a quadrupole aerosol mass spectrometer (Q-AMS) at the Mace Head Atmospheric GAW Research Station, on the west coast of Ireland. Together with other real time measurement techniques operated at this station Q-AMS registered volcanic sulfate and dust plumes from Iceland in air advected over the North Atlantic Ocean. Following this event, elevated levels of sulphate and light absorbing particles were encountered at Mace Head. Concurrently nitrate levels remained low and largely unchanged indicating no major contributions from anthropogenic pollution. Advection of sulphate aerosol formed from direct sulphur emissions from volcanoes caused significant changes in the aerosol chemical composition and size distribution. A concurrent dust outbreak from Iceland increased the level of absorbing material. These results suggest that volcanogenic emissions and Aeolian dust from Arctic deserts in Iceland can be potentially significant regional sources of aerosols over the North Atlantic and therefore should be adequately considered in regional and global climate models.

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Microbial population structure at low-temperature siliceous Fe-deposits at the Jan Mayen hydrothermal fields

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Large amounts of siliceous Fe-hydroxides are deposited by low-temperature hydrothermal venting distal to the high-temperature vents at the southwestern part of the Mohs Ridge close to Jan Mayen. The deposits occur as rust coloured mounds and small chimney-like structures along faults and fissures in the rift valley for distances of several hundreds of metres. The deposits have a stratified structure of millimetres to centimetres thick yellow to dark brown laminated layers that are separated by millimetres to centimetres sized cavities. The individual layers and lamina have a highly porous microtexture of various filamentous particles. The dominating particles in brown layers are 1 µm thick tubular and flat, twisted and branching filaments resembling stalks of iron-oxidising bacteria like *Gallionella sp* and the newly described *Mariprofundus ferrooxidans* that are encrusted by various amounts of Fe-hydroxide.

The analytical power of environmental DNA sequences for modelling microbial ecosystems depends on accurate assessments of population structure. Clone library and 454 pyrosequencing was therefore used to estimate the number of operational taxonomic units (OTU) in these iron rich structures. Phylogenetic analyses evidenced a large diversity of uncultured bacteria where proteobacteria (55%) and planctomycetes (16%) were the numerically abundant groups. There is limited knowledge about iron oxidation as an ancient metabolic pathway and few isoaltes have so far been cultivated. To further investigate the role of this iron mounds into the ecosystems and their interaction with microorganisms, cultivation experiments focusing on enrichment of iron oxidisers using FeS as substrate were applied. Dominant members in the enrichments showed closest phylogenetic affiliation (97% identity) to the newly described *Mariprofundus ferrooxidans* which is a novel lineage of ζ-proteobacteria involved in formation of marine biogenic iron precipitates. The most abundant OTU within the ζ-proteobacteria however shows phylogenetic affiliation to a novel organism present in our enrichments.

Simulated microstructure development during prograde metamorphism

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Rocks undergo progressive changes in mineralogy, mineral composition, and microtexture during metamorphism. Changes in mineral assemblage and composition can be readily predicted by equilibrium thermodynamics, but textural maturation is currently not easily predictable. Textures that are common to many rocks that experienced similar *P-T*-time histories, indicate which key internal processes control formation of these textures.

Here we model the porphyroblast and matrix texture, and chemical zoning formed during a prescribed metamorphic path, deducing the ranges of significant external parameters (chiefly temperature range, rate of change of temperature, and metamorphic duration) that produce final textures comparable with natural examples. Petrographic observations to be matched include the range of crystal sizes within a single sample, the spatial distribution of crystals of any specific phase, the chemical zoning of crystals as a function of crystal size, and the lengthscale of chemical equilibrium between multiple grains.

We focus on isobaric prograde metamorphism, analogous to heating of pelitic rocks due to a proximal magmatic intrusion. This allows a large ΔT and easily predictable timescale, without necessarily introducing significant deformation. Diffusion of certain important elements (Mg, Fe, Ca, Mn) within crystals and along grain boundaries has been tracked, and crystal growth due to changing temperature has been permitted. Preliminary results indicate that with simple modifications of ELLE [1] experiments, realistic rock microtextures can be simulated for geologically consistent parameter ranges.

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Genetical modelling of the epithermal Hg deposit of Halıköy, Sb deposit of Emirli and Au deposit of Küre in the rift zone of the Küçük Menderes, Western Anatolia, Turkey

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From Early to Middle Miocene, the continental rift zones of the Büyük Menderes, Küçük Menderes and Gediz within the Menderes Massif were formed by extensional tectonic features, which strike E-W generally and are represented by a great number of thermal waters, epithermal mineralizations and volcanos with ages up to 18.000a. The thermal waters and epithermal mineralizations are related to faults which strike preferentially NW-SE and NE-SW and locate diagonal to general strike of the continental rift zones. These faults are probably generated by compressional tectonic stress which leads to deformation of uplift between two extensional rift zones.

The Hg deposit of Halıköy, Sb deposit of Emirli and Au deposit of Küre are located in the eastern part of the continental rift zone of the Küçük Menderes within the Menderes Massif in Western Anatolia, Turkey. The ore mineralizations of these three deposits is associated with Paleozoic altered mica schists. At the surface, the host rocks are intensively altered by interaction with the circulation of geothermal fluids. Therefore, the ore fields can be recognized by a distinct color change of the rocks. The hydrothermal alteration is noticeable at the surface which is distinguished by phyllic, argillic and silicic alteration zones.

The isotope ratios of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in fluid inclusions of quartz samples of Halıköy, Emirli and Küre show a similarity with active geothermal systems. By using geological, geochemical, isotope geochemical, ore and rock microscopical and microthermometric methods these deposits in the rift zone of the Küçük Menderes have been modelled genetically and can be considered as fossil geothermal systems.