## Sulfur speciation in natural geothermal fluids, Iceland –

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Kinetically or thermodynamically

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General redox dis-equilibrium often prevails in natural geothermal waters [1]. Sulfur has a complex redox chemistry and is among the major components in geothermal fluids. Its most common redox states are sulfate (VI) and sulfide (-II), but metastable species with intermediate oxidation states have been found to be sometimes present in significant concentrations in contrast to thermodynamic considerations in surface geothermal waters. The concentrations and origin of the intermediate species are not well understood and so far unknown for the deeper parts of geothermal systems.

Sulfur chemistry was studied in surface geothermal waters such as hot springs, acid-sulfate pools and mud pots as well as deep aquifer fluids discharged by sub-boiling and two-phase wells in Iceland. The speciation of aqueous dissolved sulfur (sulfide, sulfate, sulfite, thiosulfate and polythionates) was determined on-site or after sample stabilization in more than 60 samples. Sulfate was identified in all samples in concentrations between 0.2 to 53 mmol kg<sup>-1</sup>, and sulfide in most waters with few exceptions ranging between 0.3 to 4100 µmol kg<sup>-1</sup>. Sulfite was not detectable in most samples, but was found in some surface geothermal waters associated with high sulfide concentrations. Thiosulfate was detected in most samples in concentrations ranging from 1.2 to 394 µmol kg<sup>-1</sup>. Thiosulfate and sulfite were not present in the deeper parts of subboiling systems and in low concentrations (<10 µmol kg<sup>-1</sup>) in higher temperature systems. Polythionates were not detected.

The results indicate that the sulfur speciation in natural geothermal waters is kinetically and/or source controlled rather than thermodynamically. In the deeper parts of volcanic geothermal areas, the sulfur redox equilibrium is more closely approached. The aqueous speciation of sulfur is very complex and dynamic, and can not be estimated from bulk analysis and measurements of a given redox state. This has implications also on the chemistry of other elements associated with sulfur species.

[1] Stefánsson et al. 2005. Chem. Geol. 221, 289–311.

## The influence of irradiation and aging on nano-iron versus its bulk analogue in natural seawater

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Engineered nano-iron is widely used in bioremediation and also in the food industry. Experiments were designed to expose organisms to equimolar "surfce-bound"  $Fe^{3+}$  from both the nano-form (Fe<sub>2</sub>O<sub>3</sub>) and its bulk analogue (FeCl<sub>3</sub>), to study the impact on early life stage development of marine invertebrates. The influence of the aging of particles and elevated UV-B on suspensions in seawater were studied. Iron nano particles were characterised using an array of techniques including dynamic light scattering (DLS), X-ray diffraction (XRD), nanoparticle tracking analysis (NTA), filterfractionation followed by inductively coupled plasma optical emission spectrometry (ICP-OES), atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), etc.

Preliminary results obtained when comparing the two forms of the metal indicate clear differences in particle aggregation behaviour, hydrodynamic diameter, polydispersity index, zeta potential and particle surface topography. Results are valuable to explain differences observed in biochemical responses in test organisms.

This work aimed to differentiate between nano-form related biochemical responses as compared to effects from bulk analogues, and thus generates much needed risk data to support evidence based nanoparticle regulation.

## Behavior of Silver nanoparticles in a waste water treatment plant

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Metallic silver nanoparticles (Ag-NP) are increasingly used as biocides in a wide range of products. Because Ag-NP will mainly be released into sewer systems, retention of Ag-NP in wastewater treatment plants (WWTP) will control the extent to which Ag-NP are released into the aquatic environment. Physical and chemical processes during aerobic and anaerobic stages of wastewater treatment may change the speciation of Ag and the colloidal stability of the Ag-NP and thereby the degree of Ag-NP retention in the WWTP.

We investigated the fate of the Ag-NP during wastewater treatment in a pilot scale WWTP consisting of a non-aerated tank (7m<sup>3</sup>), an aerated tank (7m<sup>3</sup>) and a secondary clarifier (11m3). Real municipal wastewater (24m3/day) was spiked with Ag-NP to reach an Ag concentration of 130 µg/l in the influent. The experiment consisted of an initial dosage (1day, 2.4 g/l Ag at a flow rate of 1 l/h, i.e. 57.6 g/d Ag) followed by 24 days (twice the sludge age) of continuous Ag-NP dosage (3.1 g/day) and 24 days of normal operation without Ag-NP addition. Samples from the sludge and from the effluent were collected for analysis. Inductively coupled plasma mass spectroscopy (ICP-MS), X-ray absorption spectroscopy (XAS) and electron microscopy (SEM, TEM), were used i) to establish the mass balance of the total Ag, ii) to determine bulk Ag speciation in the sludge and iii) to determine the agglomeration state of the Ag-NP and their transformation products.

XAS and TEM analysis of the starting material confirmed that the Ag-NP were metallic and <15nm in diameter. The mass balance derived from the ICP-MS analyses demonstrated that about 5% of the Ag-NP passed the WWTP. TEM analyses of the effluent revealed that the Ag-NP passing the WWTP were mostly attached to or incorporated into micron-sized flocs. Further XAS analyses will be performed to determine the speciation of Ag in the sewage sludge and TEM analyses on resin-embedded thin-sections will provide additional insight into the interaction of Ag-NP with bacteria and decomposing organic material in the sludge. This study provides a robust mechanistic and quantitative basis for future studies on Ag-NP emissions and exposure in aquatic systems and will be very important for future risk exposure studies of Ag-NP.

## Pushing the limits of neutron tomography

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Neutron tomography of dynamic processes requires special care and planning of the experiment. This is a challenge due to the long scan times which are in the same order as the time constant of the studied process. Too fast processes will result in motion artifacts.

There are several points of the experiment that can be modified to decrease the scan times of a sample. In general, increased temporal resolution comes at the price of lower spatial resolution. Here, an overview of the efforts to increase the temporal resolution made at the neutron imaging beamlines ICON and NEUTRA (Paul Scherrer Institut, Switzerland) is reported.

A basic method to decrease the exposure times is to increase the neutron flux. If this is possible at all, it usually comes at the cost of reduced beam collimation. On our beamlines we are working on increasing scintillator efficiency and shortening the readout times from the acquisition devices. A method to shorten the scan and readout times is to use binning and cropping, i.e. reducing the spatial resolution of the projection data. This has the side-effect that less projections are required to fullfill the sampling theorem [1].

Currently, filtered back-projection is the main reconstruction method. However, to reduce the number of projections other reconstruction methods are required. E.g. [2] used a penalized likelihood method to reconstruct image using 46 projections. A different approach is to use tomosynthesis, i.e. only reconstructing a vertical slab using few projections and short scan range. This method is advantageous for samples with complex tubing.

By continuous development of the beamlines we are mostly able to meet the requirements of the user community.

[1] Kak & Slaney (2001) Principles of computerized tomographic imaging, SIAM. [2] P. Trtik et al. (2010) Int. Conf. on Material Sci. & 64th RILEM September 6–10, Aachen, Germany, (submitted)

## Interactions of organic matter with minerals – Ultimate stabilization in soils?

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All organic matter (OM) in soil derives from primary production, i.e. from leaves and roots. The initial decomposition of these primary sources depends largely on their chemical properties with recalcitrant aromatic constituents being more resistant. Since intrinsically labile compounds also accumulate in soils, we have to address the factors that add to the observed stabilization of compounds spanning a wide range of intrinsic stabilities.

Adsorption of OM to pure mineral surfaces and its (co-) precipitation with amorphous Fe and Al phases and metals mostly result in preferential enrichment of lignin-derived aromatic compounds. This fractionation along with the formation of strong innersphere complexes between mineral surfaces and OM may be the key process in the stabilization against microbial decay. Weak mineral–organic bindings are favored at a small availability of sorption sites where other solution constituents like phosphate effectively compete with OM. In this case, N-rich, less aromatic and less complex OM accumulates selectively, resulting in minor stabilization of bound OM [1].

Factors supporting the stabilization of sorbed OM in soil include (i) the surface area and reactivity of minerals, (ii) the inherent stability of OM, and (iii) strong bonds decreasing its desorption as a precondition for microbial utilization [2]. The stability of sorbed OM seems to be largest in the mineral subsoil because of the availability of bare and reactive minerals irrespective of the intrinsically labile character of OM. Despite small  $\Delta^{14}$ C values of subsoil OM, the accumulation of microbial residues and a continuous production of dissolved OM indicate ongoing C turnover also in such 'high-stability environments'. This is supported by the results of incubation experiments. Therefore, interactions of OM with minerals do not result in ultimate stabilization and the usefulness of <sup>14</sup>C as a universal measure of C stabilization might be questioned.

[1] Schneider *et al.* (2010) *GCA*, in press. [2] Mikutta *et al.* (2009) *GCA* **73**, 2034–2060.

## Molecular mechanisms of the librational motions of water in the interlayers of hydrocalumite

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Hydrous interlayers of layered double hydroxides (LDHs, anionic clays) can contain  $H_2O$  molecules and a wide variety of anions which often occupy well-defined structural positions and coordinations. Hydrocalumite, also known as Friedel's salt,  $[Ca_2AI (OH)_6]CI\cdot 2H_2O$ , has a well-ordered Ca, Al distribution in the hydroxide layer and a particularly high degree of  $H_2O$ , Cl ordering in the interlayer. Thus, is represents an excellent model system for detailed molecular-level studies of the structure and dynamics of nano-confined water in minerals.

We used molecular dynamics (MD) simulations and quasielastic neutron scattering (QENS) to investigate the dynamics and mechanisms of  $H_2O$  librational and reorientational motions in the hydrocalumite interlayers at temperatures above and below the previously discovered order-disorder interlayer phase transition. The experimental and MD modeling results are consistent in capturing the important details of the dynamics of nano-confined water and the effects of the orientational ordering of the interlayer  $H_2O$  molecules. Unexpectedly, the MD simulations also reveal that the dominant mechanism of  $H_2O$  reorientation is not the rotation in the plane of the molecule, but a 'flipping' motion in which one hydrogen bond to a neighboring interlayer  $CI^-$  ion remains intact, while another H-bond changes its coordination between two other neighboring  $CI^-$  ions.

The combination of QENS and MD approaches provides new otherwise unobtainable information, significantly adds to our current understanding of the  $H_2O$  structure and dynamics in LDH phases, and can now be extended to probe the dynamics of nano-confined and interfacial water in more disordered phases (LDH, clays, cement, etc.), for which much less initial structural information is available. S.N. KALMYKOV<sup>1</sup>\*, O.N. BATUK<sup>1</sup>, M. BOUBY<sup>2</sup>, M.A. DENECKE<sup>2</sup>, A.P. NOVIKOV<sup>3</sup>, I.V. PERMINOVA<sup>1</sup>, AND N.S. SHCHERBINA<sup>4</sup>

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Production Association 'Mayak' is the facility that is responsible for spent nuclear fuel reprocessing, isotope production and radioactive waste management. For decades it was also responsible for the separation of plutonium for military purposes. As a result of activities in 50's and 60's of XX century, large surface and subsurface contamination by different radionuclides occurred. In this study plutonium speciation in bottom sediments and water from natural open reservoirs is reported by various methods including TEM, SEM-EDX, sequential extraction and AsFFF coupled with organic carbon analysis and ICP-MS.

According to plutonium inventory in different reservoirs, its major fraction (>90 %) is in the bottom sediments from the reservoirs. According to the sequential extraction the partitioning of plutonium is governed by the interaction with high molecular weight natural organic matter (NOM) in the bottom sediments.

Despite most of Pu was found in the bottom sediments, small fraction of this element was also found in water. Its speciation was analysed by various methods including Assymetric Field Flow Fractionation coupled with total carbon analysis and ICP-MS. It was established that Pu was bound to stable nanocolloids with the hydrodynamic diameter of 1-2.5 nm. This corresponds to the fraction of low-molecural weight NOM, presumably fulvic acids. The separate sampling was done to separate emough amount of this NOM for STXM and C-13 NMR examination that confirmed that this fraction correspond to aquatic fulvic acids. The AsFFF separation also indicate the presence of the NOM with the hydrodynamic diameter of 8-15 nm, but no plutonium was detected bound to this fraction.

## Steady-state U-series systematics recorded in two deep weathering profiles, India

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Weathering exerts a profound influence on the elemental and isotopic inventories of nutrients in the ocean. Whilst many laboratory experiments have provided a rationale for preferential release or retention of elements or isotopes, empirical studies of deep weathering or lateritic profiles, and suspended sediment have returned more complex answers. This situation is also true for <sup>234</sup>U, whose activity in the ocean is elevated yet few weathering studies have succeeded in documenting the complementary <sup>234</sup>U-depleted residuum.

We present a new comprehensive major, trace element and U-series isotope study of two deeply weathered profiles developed across superimposed (c. 65 Ma) basaltic lava flows in the NE Deccan region of north-central India (c. 22°N, 79°E). In the upper profile, the chemical index of alteration (CIA) correlates strongly with loss on ignition ( $r^2 = 0.972$ ). The lowest CIA of 40 is found in the centre of unweathered corestones and increases both upwards to the thin soil and downwards to the contact with the lower flow. High-precision trace element data show fine-scale but significant and correlated variations in element ratios such as La/Gd, Eu/Eu\* and Y/Ho. By contrast, high-field strength elements (HFSE) are only mildly affected by weathering, and Th/U has remained relatively constant (4.04±0.71) across the profile.  $(^{234}U/^{238}U)$  ranges from 0.79 in the most weathered samples, to 1.01 in the unweathered basalt, showing only weak correlation with CIA and LOI. Preferential <sup>234</sup>U loss is strongly correlated to  $^{230}$ Th loss (r<sup>2</sup> = 0.841) along the  $^{234}$ U/ $^{230}$ Th equiline suggesting young steady state behaviour.

The lower profile is more homogenously weathered, with CIA ranging from 0.71 to 0.79, whilst Y/Ho is consistently subchondritic (22.5±0.34) similar to that of the most strongly weathered samples in the upper profile. HFSE are also fractionated: both Zr/Hf and Nb/Ta increase downwards through the profile, whilst Th/U is generally higher than in the upper profile, ranging from 4.8 to 7.4, indicating a general loss of U. U-series confirm strong disequilibria with ( $^{234}U/^{238}U$ ) ranging from 0.53 in the more weathered samples to 0.97, and is remarkably strongly correlated with depth ( $r^2 = 0.981$ ). Again,  $^{234}U/^{230}$ Th equiline.

In both flows, preferential weathering occurs towards the lower flow contacts. Young, steady-state loss of daughter nuclides confirms experimental studies regarding preferential solubility and, unlike data for suspended sediment, provides an explanation for the <sup>234</sup>U excess in river and seawater.

## Reliability of LA-MC-ICP-MS Hf isotope analyzes: Insights from natural and synthetic zircons

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In situ Hf isotopic measurements by LA-MC-ICP-MS typically require significant Lu and Yb isobaric interference corrections. To assess the viability of atomic isobaric corrections on Hf isotopic measurements, we prepared synthetic zircons with variable REE contents. Analyses of these zircons and natural zircons (91500, BR266, MAD, SAME, FC-1, and R33) using our Nu Plama show that accuracy and precision of Hf isotopic measurements decrease systematically with increasing REE/Hf ratios. The synthetic zircon experiments indicate that at Lu-Yb/Hf ratios resulting in around 20 percent or less correction between uncorrected and Lu-Yb corrected 176Hf/177Hf ratios, we can routinely obtain accurate and precise Hf isotopic data. Systematically more inaccurate and imprecise Hf isotopic data are observed at progressively higher correction levels. Our experiments show that at lower REE/Hf the REE oxide interferences on the masses of interest are, to a certain extent, self-cancelling and do not affect the Hf measurements at the 1 eHf level (2s). Above the ~20% correction threshold, however, the REE oxides differentially affect a number of ratios used in the Hf isotope data reduction protocol. As a result, Lu-Yb peak stripping based on atom % of the constituent isotopes becomes a progressively less adequate proxy for all isobaric interferences. For example, R33, which has relatively high REE/Hf ratios compared to FC-1, suffers in both accuracy and precision (± 2 eHf 2s, on average) vs. FC-1 (1 eHf 2s). Our experiments support previous suggestions of the ~20% correction limit and directly tie this limit to REE oxide formation. Unfortunately, the formation of these oxides appears to be too irregular to apply accurate corrections at higher correction percentages, which suggests that their production reflects multiple modes (e.g. during ablation, ionization, and transfer from the plasma to the mass spectrometer). Consequently, the extent of oxide production and limit of viable correction is likely to be dependent to some degree on instrumental and experimental conditions as well as target composition.

## Mechanism of selenite sequestration by low-soluble phosphate minerals

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Selenium-79 (the half-life of  $6.5 \times 10^4$  yrs) in high-level radioactive waste needs to be safely disposed in geological repository. However, Se has low affinity against various sorbents due to the common anion species such as selenite  $(SeO_3^{2-})$  and selenate  $(SeO_4^{2-})$ . On the other hand, apatite was proposed as an efficient sorbent for anion species as well as Pb salt of Se oxoacid with low solubility. In order to understand the mechanism of Se sequestration by apatite and pyromorphite in the Se-Pb-P-O system, we have conducted sorption experiments under four conditions: (*i*.) hydroxylapatite (HAP, Ca<sub>5</sub> (PO<sub>4</sub>)<sub>3</sub>OH) reacted in 0.5 mM Na<sub>2</sub>SeO<sub>3</sub> solution at initial pH of 5.0 or 9.5; (ii.) hydroxypyromorphite (HPY, Pb<sub>5</sub> (PO<sub>4</sub>)<sub>3</sub>OH) reacted in 0.5 mM Na<sub>2</sub>SeO<sub>3</sub> solution at initial pH of 5.0; (iii.) HAP reacted in the solution with 0.5 mM  $Na_2SeO_3$  and 0.5 mM Pb  $(NO_3)_2$  at initial pH of 5.3. All experiments were carried out at room temperature for 30 min. to 30 d. Analytical technique includes an inductively coupled plasma-atomic emission spectrometry (ICP-AES), a powder X-ray diffraction analysis (XRD), and transmission electron microscopy (TEM).

In the condition (i.), Se concentration in solutions did not change significantly during the reaction and the XRD shows no peak besides HAP peaks at both pHs, indicating that Se sorption proceeds by surface adsorption in addition to anion exchange. HAP seems not effective sorbent under this experimental condition due to its limited number of Se adsorption site on the HAP surface. In case of (ii.), XRD patterns show peaks of molybdomenite,  $PbSeO_3$ ,  $P2_1/m$ , z = 2. The concentration of Se decreased from 0.49 mM to 0.30 mM in 30 d, while P concentration gradually increases to 0.06 mM, indicating the formation of PbSeO<sub>3</sub> as a consumption of Pb<sup>2+</sup> released from HPY dissolution. In the condition (iii.), PbSeO<sub>3</sub> with structure of  $P2_1/c$  (z = 8) precipitated in the solution prior to contact with HAP. Both Se and Pb concentrations decreased from 0.05 mM and 0.10 mM to under detection limit. Moreover, TEM reveals that Pb and Se nano-needles  $(40 \times 10)$ nm) formed epitaxially on the tip of HAP.

These results suggest that the form of sequestered Se is largely dependent of the combination of the initial form of  $Pb^{2+}$  and the template crystals. Consequently, Se sequestration is constrained by complex kinetic processes between different forms of Pb selenite in the presence of low-soluble Pb-phosphate.

## Oxygen isotope ratios in mantle xenoliths (Mt. Carmel, Israel): Implications for thermometry and sources of alkaline mafic magmas

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A suite of rare mantle pyroxenite xenoliths occurs within Upper Cretaceous mafic pyroclastic sections at Mt. Carmel, northern coastal Israel. The suite solely includes garnet clinopyroxenites with abundant indicating crystallization at P > 2 GPa [1].  $\delta^{18}$ O values of clinopyroxene (Cpx) and garnet (Grt, Pyr<sub>60</sub>Alm<sub>30</sub>Grs<sub>10</sub>) from 9 xenoliths range from 4.99 to 5.42‰ and 5.14 to 5.47‰, respectively. All laser fluorination analyses were duplicated with average duplication difference of 0.03‰ for Grt and 0.05‰ for Cpx;  $\delta^{18}O_{CDX}$  values were corrected according to [2]. Isotope fractionations are  $\Delta^{18}O_{Cpx-Grt} = -0.22$  to 0.07%, averaging -0.08  $\pm$  0.06% (2SE). The Carmel negative Cpx-Grt fractionations (7 out of 9 xenoliths) are outside the ovewhelmingly positive  $\Delta^{18}O_{Cpx\text{-}Grt}$  range of 0.0 to 0.6‰ measured in 62 worlwide 'eclogitic' mantle xenoliths [3]. The experimental calibration of diopside-grossular fractionations predicting  $\Delta_{\text{Di-Grs}}$  = 0.17‰ at 1000°C is not applicable here due to the Mg-Fe composition of the garnet. However, calculations based on natural samples predict  $\Delta_{\text{Di-Ca-poor Grt}} \ (1000^\circ\text{C})$  to be -0.06 [2] or -0.02 [4]. If equilibrated, our results extend to T  $\approx$ 1100°C, further showing that for the vast majority of igneous and metamorphic rocks diopside-Ca-poor garnet equilibrium fractionation is  $\approx 0\%$  and insensitive of temperature. The 0.6‰ variability in  $\Delta^{18}O_{\text{Cpx-Gr}}$  measured in mantle eclogites [3] may stem from differences in chemical composition, late alteration and analytical precision. Garnet megacrysts (<10cm) that also occur within the pyroclastic sections have chemical composition and  $\delta^{18}O$  (5.43  $\pm$  0.06‰) similar to the granoblastic garnet (3-4mm) in the xenoliths. This suggests that metamorphic recrystallization of the pyroxenites prior to uptake by magma did not involve metasomatism by exotic fluids.

[1] Mittlefehldt (1986) *CMP* **94**, 245–252. [2] Kohn & Valley (1998) *JMG* **16**, 625–639. [3] Mattey *et al.* (1994) *EPSL* **128**, 231–241. [4] Valley (2003) *Rev. Min. Geochem.* **53**, 343–385.

## Coupled CO<sub>2</sub>-leakage and *in situ* fluid-mineral reactions in a natural CO<sub>2</sub> reservoir, Green River, Utah

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Surface travertine deposits and carbonate veining within the footwall of Little Grand Fault and Salt Wash Graben, Utah, record a 413 ka history [1] of CO<sub>2</sub> leakage [2]. Isotopic analysis of U-series dated carbonate veins reveals a coupling between CO<sub>2</sub> injection into the host aquifer and the rates of surface leakage, CO2-promoted silicate mineral hydrolysis reactions within the reservoir [3] and carbonate deposition within fracture conduits through which CO<sub>2</sub>-charge fluids ascend to the surface (Fig. 1). Rapid carbonate precipitation rates, recorded in the kinetic fractionation of  $\delta^{13}C_{HCO3}$  and  $\delta^{18}O_{HCO3}$ , reflect an increase in *in situ* pCO<sub>2</sub> which elevates concentrations of Ca<sup>2+</sup> and HCO<sub>3</sub>, lowering the point at which the ascending fluid reaches carbonate supersaturation due to CO<sub>2</sub> degassing. The spatial and temporal relationship of travertine deposition to CO<sub>2</sub> injection, suggests that rapid rates of carbonate deposition initially plug easily exploited leakage pathways causing leakage sites to propagate laterally, but that this blocking rate decreases with dissipation of the CO<sub>2</sub> charge. This has important implications for the prediction of leakage behaviour in storage sites and for modeling the coupling of subsurface geochemical processes to the evolution of surface leakage.



[1] Burnside *et al.* (2009) in Faults & Top seals, EAGE. Montpellier, France. [2] Dockrill *et al.* (2010) J. Struc. Geol. in press [3] Kampman *et al.* (2009) Earth Planet. Sci. Lett. **284**, 473–488.

## Solubility of cycloctasulfur in water as a function of temperature, salinity and sulfide concentration

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Cycloctasulfur and inorganic polysulfides are important sulfide oxidation intermediates and bacterial substrates. Solubility of rhombic sulfur ( $\alpha$ -S<sub>8</sub>) in water was studied as a function of temperature by derivatization with hot hydrogen cyanide solution followed by HPLC-UV analysis of formed thiocyanate [1]. Sulfur solubility in pure water was found to increase with temperature from 6.1 nmol l<sup>-1</sup> S<sub>8</sub> at 4<sub>i</sub>C to 478 nmol l<sup>-1</sup> S<sub>8</sub> at 80 iC. Solubility of sulfur in sea water was found to be 61±13% of the solubility in pure water regardless of the temperature [2]. Results of this work are in good agreement with reported values for solubility of  $\alpha$ -S<sub>8</sub> in water at 25<sub>i</sub>C [3, 4]. In the presence of hydrogen sulfide and its deprotonated forms the solubility of cyclooctasulfur in water increases due to formation of polysulfides (1) [5].

 $HS^{-} + (n-1)/8 S_8 = S_n^{2-} + H^{+}$ 

At pH values of 8.2, 7.0 and 4.3 polsyuflidic zero-valent sulfur dominates over dissolved  $\alpha$ -S<sub>8</sub> at [S (II)] > 0.5  $\mu$ M, 5  $\mu$ M and 300  $\mu$ M respectively.

(1)



**Figure 1.** Solubility of cyclooctasulfur  $S^0$  and polysulfide (PS)  $S^0$  at infinite dilution.

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# On the **D**ipole CHIMÕtechnique electrified by low voltage dipole

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Concealed deposits are dissolved in electrogeochemical forms. Metal anionic and cationic species of elements migrate to near the surface driven by all kinds of geological forces, and are enriched therein. The metal ions of electromobile forms are extracted in either anodes or cathodes with the aid of artificial electric field, which are called CHIM anomalies [1]. CHIM ionic haloes, dynamically related to concealed deposits, are in mobile form. The element composition of the haloes is normally the same as that of the ores, and the haloes occur typically directly over the source of the deposits [2, 3]. With this new halo-forming theory [1], the extract tests with the single cathode electrified by low voltage QuipoleOwas first carried out at several known mine areas, and their feasibility and effectiveness were verified [4]. Recognizing that anionic as well as cationic species may provide useful information [5], Dipole CHIMÕtechnique electrified by low voltage dipole was then proposed and developed. Field tests of this innovative technique were undertaken with great success, which had enabled us to identify clearly multi-element anomalies at Yingezhuang gold deposit in Shandong, at 210 gold deposit in Xinjiang and at Jinchuan copper-nickel deposit in Gansu. The test results indicate that anionic species anomalies of elements are very obvious above the existing ore bodies, and the sum of anionic and cationic species anomalies enables the identification of the position of the deeply buried ore bodies. This new CHIM technique, characterized by simple equipment, easy operation and low cost, enables simultaneous extraction of anionic and cationic species of elements, from which more information can be derived with higher extraction efficiency. This technique is therefore suitable particularly for field surveys.

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## Remediation of TCE-contaminated groundwater using nanocatalyst and bacteria

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Nano-bio-technology has the potential to create novel and effective treatment technologies for groundwater remediation. The objective of this study was to develop and evaluate remediation of TCE-contaminated groundwater using both nanocatalyst (biomagnetite) and bacteria (mostly *Clostridium* sp.) in anoxic environments.

Four columns (43 cm long and 7 cm internal diameter) packed with synthetic silica beads with diameter of 1 mm were used in anoxic environments: (1) control column, (2) bacteria inoculated column, (3) nanocatalyst inoculated column, and (4) both nanocatalyst and bacteria inoculated column. TCE contaminated water was injected from the bottom of the column using peristaltic pump at constant flow rate.

In the case of the control column, 50% natural reduction of TCE was observed within 5 days of the column experiments. The column tests confirmed that the application of bacteria, nanocatalyst and both nanocatalyst and bacteria showed 100% TCE dechloination within 4 days of the column experiments. The TCE dechlorination mechanism appeared to be reductive dechlorination, with electrons supplied by the magnetite oxidation and microbial oxidation of organics. These results suggested that application of nanocatalyst and bacteria has potential to create novel and effective treatment technologies for TCE-contaminated groundwater.

### Phosphate Sorption on TiO<sub>2</sub>

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Dissolved phosphorus has been the subject of interest in natural sciences because of its potential roles in ecosystems and its mobility in near-subsurface environments such as soils and groundwater. Partitioning of the phosphate to minerals such as metal-(hydr)oxides has been known to influence the surface reactivity of minerals and the fate and transport of phosphate species in natural ecosystems. Despite the importance of phosphate interaction with minerals and biological materials like  $TiO_2$  in ecosystems and medicine, the mode of phosphate uptake by  $TiO_2$  is still not clearly understood. Moreover, no direct confirmation of modes of phosphate interaction with  $TiO_2$  has been provided, especially in a molecular level.

Systematic studies, combined batch experiments with NMR spectroscopic methods, have been used to evaluate phosphate sorption on TiO<sub>2</sub>. Results show that phosphate sorption on TiO<sub>2</sub> decreases with increasing pH, whereas the phosphate uptake by TiO<sub>2</sub> increases with increasing ionic strength of the solution. In  $I \le 0.1$  M, the sorption sharply increases and reaches a near maximum and then followed by little changes showing Langmuir type behavior, whereas in I =0.7 M non-Langmuirian uptake becomes evident as equilibrium phosphate concentrations increase in solution. <sup>31</sup>P{<sup>1</sup>H} CP/MAS NMR results show that the local environment of phosphate sorbed at the TiO<sub>2</sub> surface is very similar. Spinning side binds (SSBs) suggest that the phosphate sorbed on TiO<sub>2</sub> forms inner-sphere adsorption surface complexes with Ti atoms at the surface under the conditions of our experiments. Upon <sup>31</sup>P-<sup>1</sup>H distance at 1.98 Å and 1.95 Å for two at  $\delta = -2$  and  $\delta = -9$  ppm, CP dynamics indicates that protonated phosphate species is dominant at pH 4.5, whereas deprotonated phosphate at the TiO<sub>2</sub> surface becomes evident at pH 9.0.

## Groundwater Iodine-129 speciation and its causes for release from a subsurface burial basin

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In 1989 the F-Area Basin at the Savannah River Site (SRS) containing acidic radiological waste from plutonium extraction activities was closed by adding lime and reducing slag (containing ferrous and sulfide compounds) and backfilling the basin with sediment and covered with a lowconductivity clay cap. Since 1991, 129I groundwater concentrations have been slowly increasing from ~180 to >800 pCi/L. During this same period, the groundwater pH has increased from 3.10 to 3.95 and tritium concentrations have declined from 27, 000 to 500 pCi/mL, the latter representing primarily dilution and some decay. Laboratory studies were undertaken to understand why 129I is releasing from the basin. SRS subsurface sediments were found to have a net positive charge within the acid plume (pH 3 to 5.5) and as such, had an anion exchange capacity for adsorbing the anionic iodine. The point-of-zero-charge of the study sediment was 4.0 to 4.2. As the pH of the sediment increased from about 3.1 to 3.95, sorption decreased by 24%, causing the release of iodine into the aqueous phase. Laboratory pH-iodine sorption trends and the field data of 47 <sup>129</sup>I samples over 19 years showed similar pH trends, suggesting similar processes. Additional laboratory data showed that there was a strong inverse relation to aqueous iodide concentration and degree of sorption, even down to µmolar concentrations. This finding may have uncovered previous experimental artifacts in our laboratory and elsewhere in the literature, leading to underestimation of iodine sorption. Iodate sorbed more strongly than iodide. We have quantified the presence of multiple 129I species in groundwater samples collected in a riparian zone located ~1 km from the F-Area Basin, including: colloidal iodine, organo-iodine, iodate, and iodide. These studies underscore the importance of understanding that iodine has a complicated speciation in terrestrial environments and it is necessary to study radio-iodine environmental chemistry at ambient concentrations. Studying iodine geochemistry at more elevated, albeit more convenient concentrations, resulted in assigning erroneously low sorption constants and missing dominent aqueous species.

## Influence of ionic strength on structure and redox activity of humic substances

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Humic substances (HS) are polymeric organic compounds present in soils and sediments and participate in abiotic and biotic redox processes. They can mediate electron transfer from microorganisms to poorly soluble Fe (III) minerals, but the geochemical parameters controlling these redox processes are unknown. In order to evaluate the effect of ionic strength, we incubated nonreduced and reduced HS at different ionic strength with Fe (III) compounds and quantified the amount of electrons transferred from HS to Fe (III). The amount of electrons transferred from reduced HS to Fe (III) strongly depended on ionic strength with more electrons being transferred with increasing ionic strength. This effect was observed for solid as well as for dissolved Fe (III) compounds (ferrihydrite, goethite, hematite, Fe (III) citrate) suggesting that differences in redox activity depended on changes of HS redox properties rather than on Fe (III) mineral surface effects. In contrast to HS, the quinone model compound AQDS showed no difference in redox activity at different ionic strengths, indicating that the ionic strength-dependent change in redox behaviour of HS was related to changes in HS structure. To identify the underlying mechanisms, we determined HS molecular sizes and found that nonreduced HS showed only minor changes in size at different ionic strengths, whereas reduced HS seemed to aggregate and form larger particles with particle sizes up to 4 µm at high ionic strength. Aggregation of reduced HS at high ionic strength was probably triggered by decreasing HS charges that we quantified via zeta potential measurements. Potentiometric titration of reduced HS showed that neither identity nor quantity of functional sites exposed were influenced by ionic strength. Our results suggest that during reduction, HS molecules expand due to an increase in intramolecular electrostatic repulsion caused by increased charge densities. This process in combination with decreasing zeta potentials at high ionic strengths favours aggregation of reduced HS molecules. The resulting large, network-like HS structures may then offer an improved access of reactive sites in HS for dissolved Fe (III) and/or exhibit a facilitated electron transfer to Fe (III). The enhanced electron transfer may be caused by increased orbital overlap within HS molecules, leading to a larger extent of Fe (III) reduction at higher ionic strength.

## The types of hydrothermal alteration and behavior trace elements at around of Eastern Black Sea Volcanites and Sulfide deposits, Turkey

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The volcanic rocks of the Eastern Black Sea are predominantly andesitic to dacitic in composition and partly composed of rhyolitic and rhyodacitic lavas and pyroclastics. Widespread and intense hydrothermal alteration associated with volcanogenic massive sulfide and vein-type sulfide deposits are observed throughout Upper Cretaceous aged rocks in the Eastern Black Sea volcanogenic province. The ore deposits are accompanied by intense potassic, phyllic (sericitic), argillic, silicic, propylitic and hematitic alteration. To investigate the effects of hydrothermal alteration on the chemistry of the volcanic rocks, in addition to mineralogical analysis the parent and altered rocks, chemical composition (major and trace elements, including rare-earth elements (REE), was analyzed.

The results of this study demonstrate notable differences in the REE behavior in the different sample groups. The potassic, hematitic, illitic and smectitic altered rock groups are characterized by moderate LREE enrichment  $((La/Yb)_{cn} =$ 8.18, 8.95, 10.49 and 11.03, respectively), while other rocks groups have slight LREE enrichment. Most of the samples have pronounced strong and/or slight negative Eu anomalies ranging from 0.35 to 0.88, while hematitic and propylitic rock samples have slight positive Eu anomalies (1.5 and 1.11, respectively). Most of samples show positive Ce anomalies, except hematitic (0.95) and smectitic (0.97) samples. Mass gains of HFS, TRT, REE and LIL elements were found in nearly all sample groups. LRE elements are generally retained in illitic and smectitic samples, while HFS and TRT elements were retained in hematitic samples and LIL elements in potassic and illitic samples.

## Introducing of alteration zones related to mineralization in Darreh-Zar area, Kerman, Iran

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The Darreh-Zar area is situated in a part of the Urumieh-Dokhtar Magmatic belt in the centre of Iran. The Eocene volcano-sedimentary rocks are the main geological units in the area. These rocks are intruded by the Oligo-Miocene intrusive bodies where they caused an intensive alteration and formation of copper mineralization.

Petrography and mineralization and XRD studies show pervasive alteration zones related to mineralization. The alterations are potassic, phyllic, argillic, propylitic and silicification. Mineralization frequently is associated to argillic and silica alteration. Also phyllic overprints with potassic alteration in the central to western parts of the area. The potassic zone includes K-feldspar, biotite and hornblende. Biotite and hornblende are frequently altered to chlorite.

The mineralization is in the form of disseminated, vein and vein let around of faults zone, dikes and intrusive missives. The main mineralization texture is open-space filling. The ore minerals are pyrite, chalcopyrite, covellite, bornite, chalcosite and galena. Copper carbonates with iron oxides are visible also frequently. Pyritization is associated mostly with pervasive altered rocks. The pyrites can be seen in the form of disseminated and vein let. Also, this zone is associated with disseminate chalcopyrites. It seems that alterations, disseminate chalcopyrites and pyrite have been formed by a primary high temperature hydrothermal fluids. Finally, the formation of carbonated and oxide minerals mostly occur on weathered surface rocks.

## First-principles simulations of structural and transport properties of silica liquid with/out water

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First principles molecular dynamics simulations show that water (8.25 wt%) has profound effects on the structural and transport properties of SiO<sub>2</sub> liquid over wide ranges of pressure (0 to 150 GPa) and temperature (3000 to 6000 K). We find that the melt structure changes substantially on compression. The speciation of the water component at low pressures is dominated by the isolated structures (with 99 % hydrogen participated) consisting of hydroxyls, water molecules, O-H-O bridging, and four-atom (O-H-O-H and H-O-H-O) groups. All hydroxyls are polyhedral (i.e. bound to Si atoms) whereas molecular water is mostly free. As pressure increases, these isolated structures increasingly combine with each other to form extended structures involving a total of five or more O and H atoms, which together consume over 75 % hydrogen at the highest compression studied. Water is shown to systematically depolymerizes the melt structure - the content of nonbridging oxygen (which is almost absent in anhydrous liquid) increased and the content of bridging oxygen decreased. Consistently, the dynamics of silica liquid is dramatically enhanced (higher diffusivities and lower viscosity) in the presence of water. At 3000 K, the diffusivities of all species (Si, O and H) and viscosity vary anomalously with pressure. The predicted dynamical changes are successfully associated with water-induced depolymerization of melt structure and water speciation, and the relevant microscopic mechanisms are revealed. Our predicted results here including those of MgSiO<sub>3</sub> liquid are expected to provide a fundamental basis for any dynamical model of magma ocean evolution.

## Correlations of H<sub>2</sub>O and S in the Martian midlatitudes

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Correlations between Mars Odyssey GRS-derived S and H<sub>2</sub>O mass fractions in the planetary surface to several decimeter depths vary hemispherically, latitudinally, and across two regions of H<sub>2</sub>O enrichment labelled 1 and 2 (Figure 1). Key observations include: (1) Areas of poor correlation (e.g. the Northern Hemisphere) contain extensive 'dust' mantles; (2) Circum-Arabia Terra (Region 1) shows the strongest correlation between H<sub>2</sub>O and S; (3) H<sub>2</sub>O and S may be weakly correlated even where H2O is enriched, as in Region 2 roughly SE of Central Elysium Planitia and W of Medusae Fossae; and (4) even where H and S are strongly correlated and ice is unstable, much of the H may not be chemically bound in sulfates. Consistent with in situ observations at Meridiani and Gusev, the computed hydration state of potential divalent sulfates is in the 1 - 3 range at regional spatial scales.



**Figure 1:** Prefix "S" denotes southern 10° - latitudinal bands, Regions 1 and 2 H-enriched regions, "R1+R2" Regions 1 and 2 combined, and "10N30S" 10° N to 30° S.

Characterization of surface properties within the two  $H_2O$  enriched regions with MRO-HiRISE imagery may help to reveal the underlying reasons for their contrasting H-S correlations. Analyses of H-Cl-S multivariate space may also clarify the potentially dominant role of non-sulfate hydrated minerals.

## A natural analogue in Southwest Wyoming for geologic co-sequestration of carbon & sulfur

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Geologic sequestration of CO2 generated by coal-fired power plants is a critical component of carbon capture and storage. Emissions from coal-fired power plants contain sulfur as well as CO<sub>2</sub>, thus successful capture and storage of anthropogenic CO<sub>2</sub> may require an understanding of geologic carbon-sulfur co-sequestration. The Mississippian Madison Limestone on the Moxa Arch, a major north-south trending anticline located in southwest Wyoming, USA, contains large amounts of supercritical CO<sub>2</sub> that it has stored naturally for millions of years, supercritical H<sub>2</sub>S, aqueous sulfur complexes (SO<sub>4</sub><sup>2-</sup> and HS<sup>-</sup>), and sulfur-bearing minerals (anhydrite, pyrite, and native sulfur). A simple equilibrium geochemical model of the Madison Limestone was constructed using mineralogic data obtained from well core and published aqueous analyses to simulate reactions among supercritical CO<sub>2</sub>, sulfur-bearing and accessory aluminosilicate minerals, and resident brine. The model accurately predicts crystallization of analcime, feldspar, and illite whereas dawsonite (NaAlCO<sub>3</sub> (OH)<sub>2</sub>), an important carbon sink in numerous sequestration modeling studies, does not occur in the Madison Limestone and was not predicted by the model. CO<sub>2</sub>-brine-rock reactions in the model Madison Limestone-fluid system decrease pH, from 6.4 to 4.0, as expected from dissolution of supercritical CO<sub>2</sub> and dissociation of carbonic acid. Redox potential increased from -0.26 to -0.06 volts due to equilibrium among CO<sub>2</sub>, anhydrite, and pyrite. Final Eh-pH conditions correctly predict the coexisting  $H_2S$ , aqueous  $SO_4^{2-}$ , anhydrite, pyrite, and native sulfur observed in produced waters and well core. The Madison Limestone serves as a natural example of the thermodynamic end point that similar fluid-rock systems will develop following emplacement of a supercritical CO<sub>2</sub>-sulfur mixture and is a natural analogue for geologic carbon-sulfur co-sequestration.

## Coalbed Natural Gas (CBNG) produced water: Geochemistry and water quality

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The CBNG extraction is facilitated by pumping water from the aquifer. The majority of CBNG produced water is discharged into disposal ponds. Water samples from outfalls and corresponding disposal ponds in Cheyenne River (CHR), Belle Fourche River (BFR), Little Powder River (LPR), Powder River (PR), and Tongue River (TR) within the Powder River Basin (PRB) were collected over a period of 10 years. CBNG produced samples were monitored pH, electrical conductivity (EC), major elements [e.g. calcium (Ca), magnesium (Mg), sodium (Na), alkalinity], trace elements [e.g. iron (Fe), aluminium (Al), barium (Ba), arsenic (As), selenium (Se)]. From Na, Ca, and Mg measurements, sodium adsorption ratios (SAR) were calculated. Results suggest that Na, alkalinity, and pH all tend to increase, possibly due to environmental factors such as evaporation, while Ca decreased from outfalls to corresponding disposal ponds due to calcite precipitation. Trace elements concentrations in both outfalls and disposal ponds were low, however an increasing trend was observed in disposal ponds (see fig. 1). Overall, these results are useful to develop management approaches for CBNG produced water and reclamation of disposal ponds [1].

> Arsenic Concentration in CBNG Produced Waters



Figure 1. Dissolved arsenic concentration in CBNG outfalls and disposal ponds.

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## Heterogenous Selenium reduction in artificial soil aggregates

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Soils display large variation with respect to their physical, geochemical and biological characteristics on scales ranging from nanometers to kilometers. The impact of this extraordinary heterogeneity on biogeochemical processes is as of yet poorly quantified and understood. In structured soils, the aggregate scale (mm-cm) is of particular interest due to the sharp transition in pore size at the surface of aggregates. Small intra-aggregate pores limit advective transport thus facilitating the formation of chemical concentration gradients that promote strong spatial variation in biogeochemical processes. One such process is the microbial reduction of Se (VI) and Se (IV) to solid Se (0). A mechanistic understanding of Se reduction within soil aggregates may lead to improved prediction of Se transport and attenuation in soils of contaminated areas.

In order to investigate the coupling of physical and biogeochemical processes controlling Se reduction at the aggregate scale, artificial soil aggregates [1] were constructed using either uncoated sand or ferrihydrite coated sand homogenously inoculated with Se-reducing bacteria (*Thauera selenatis* or *Enterobacter cloacae* SLD1a-1). Aggregates were placed in a flow-through reactor and saturated flow of aerobic or anaerobic artificial groundwater medium was initiated. Selenate and either acetate or pyruvate, for *T. selenatis* and *E. cloacae* respectively, were provided in the inflow solution. Temporal evolution of selenite and total dissolved Se was followed in the outflow solution. Concentrations of Se associated with the solid phase were analyzed in concentric sections of each aggregate.

Compared to anaerobic experiments, the microbial reduction of selenate by *T. selenatis* was severely limited, but not inhibited under aerobic conditions. Similar results were observed for *E. cloacae*, with the inhibition in aerobic experiments being less pronounced. Given that *T. selenatis* is only capable of reducing selenate to selenite in the absence of oxygen [2] and *E. cloacae* is microaerophile [3], our experimental results suggest a localized Se reduction occurs inside the aggregates under aerobic conditions for both strains of bacteria.

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## Metal stable isotope probes of electrified interfaces

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Stable isotopes are sensitive indicators of physical and chemical processes at electrified interfaces, far from equilibrium. In a series of studies [3, 4] we have derived a relationship which combines stable isotope theory and classical statistical description of electron transfer processes that predicts an isotope fractionation at an electrified interface that is dependent on the extent of thermodynami disequilibrium. In the laboratory, we have discovered a voltage-dependent isotope fractionation during electrodeposition from aqueous solutions of iron, zinc, lithium, molybdenum and copper metal. We have found that in all cases light isotopes are preferentially electroplated, with separations ranging from 0 to ~-5 ppt-large separations for isotopes of these transition metals, especially compared with those attainable using other techniques, and observed in natural environments. In addition, we have found that the isotope separations are tunable in the laboratory-by varying the plating solution, reaction kinetics, temperature (Black et al. in prep), and mass transport using the rotating disc electrode [1].

Adjacent to a charge interface, the chemical species may not have the same distribution as in the bulk solution, and an entirely different speciation may develop through the reactive intermediates involved in electron transfer processes. Therefore, the isotopic composition of the double layer will not be identical to the bulk solution, even in the absence of mass transport and electron transfer effects. Therefore, one or more intermediate species may help determine the overall isotope fractionation between a bulk solution and an electroplated product.

Here we show a joint chemical/isotope model of an electrified interace, which consideres mass transport, electron transfer, and chemical speciation. We combine theoretical models of the electrochemical double layer, with a mass-sensitive reservoir model of the reaction zone at an interface. The model predictions are compared directly with the experimental results.

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## Silicic acid removal as magnesium silicate and uptake of boron from synthetic geothermal water for the effective utilization of geothermal energy

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Geothermal energy is one of characteristic natural enargies in Japan. However, 'silica scale' and hazardous elements such as boron and arsenic included in geothermal water constitute barriers to promote geothermal power generation and utilize geothermal water. Therefore, in order to solve both silica scale and hazardous elements problems in geothermal water, silicic acid removal as magnesium siilicate and uptake of boron from synthetic geothermal water was investigated. The model experiment was conducted at ambient temperature. After magnesium was added into synthetic geothermal water (in the absence or presence of boron as 40 ppm) to have Mg/Si (moral ratio) = 1.4, 2.1, 3.5 and 4.0, pH of the solution was adjusted at 11 or 12. Sample solutions were collected after desired time and then filtrated by using 0.45µm membrane filter. Crystallinity and mineral composition of substances were analyzed by X-ray diffraction (XRD). The concentrations of silicon, magnesium and boron were determined by inductivity coupled plasma atomic emission spectrometry (ICP-AES). As increasing in Mg/Si ratio, almost all silicic acid was successfully removed from the solution at pH 11 and 12 after 24 hours (initial concentration of Si = 400 ppm). The precipitates mainly consisted of amorphous magnesium silicates. In the presence of 40 ppm boron in the synthetic geothermal solution, boron was also completely removed from the solution immediately under the condition of 2.1 or 3.5 of Mg/Si ratios at pH11. The removed boron is possibly forming amorphous magnesium borate or incorporated into the structure of magnesium silicate due to such as substitution of silicon during the formation of magnesium silicate because no boron was adhered on the surface of magnesium silicate through bonding with free hydroxyl groups. In future studies, the structure of boron incorporated by magnesium silicate should be investigated to reveal such a hypothesis.

## Quantitative evaluation of shock pressure by cathodoluminescence analysis of alkali feldspar

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Shock pressure induced on meteorites and impactites has been estimated to elucidate a meteorite ejection process based on refractive indices of plagioclase-maskelynite, which has been not available for weakly shocked materials below 15 GPa and micro-size samples. Cathodoluminescence (CL) spectroscopy provides useful information on the existence and distribution of defects and trace elements in micro-size minerals. This technique could be applied to clarify shock pressure effect on the feldspar in meteorites and impactites. In this study, CL spectral analysis of experimentally shocked sanidine has been conducted to characterize their emission mechanisms related to shock metamorphism.

**S**ngle crystal of sanidine from Eifel, Germany was selected as a starting material for shock recovery experiments at 10 to 40 GPa by a propellant gun. CL spectra were obtained by SEM-CL system, which is comprised of SEM (JEOL: JSM-5410) combined with a grating monochromator (OXFORD: Mono CL2).

CL spectrum of unshocked sanidine has an emission band at 430 nm in UV-blue region. Shocked sanidine above 20 GPa has UV-blue CL emissions at 380 and 330 nm of which intensities increase with an increase in shock pressure. The shocked samples above 30 GPa have emission bands at around 380 and 330 nm. The deconvolution of these CL spectra in UV-blue region can successfully separate the emission bands into four Gaussian components at 2.82, 2.95, 3.26 and 3.88 eV in energy units. The integral intensities of these components closely relate to shock pressure on the sanidine, suggesting CL emissions derived from shock-induced defect centers. The component intensity at 2.95 eV can be employed for the calibration to estimate shock pressure. Furthermore, this component is detected in other shocked alkali feldspar such as microcline with different structural order. Therefore, CL spectral deconvolution method allows us a new indicator for an evaluation of shock pressure in a wide range below 40 GPa for the micron-size alkali feldspar in meteorites and impactites.

## Magnesium isotopic composition of A-type granites from NW India-Asia collision zone, Xinjiang, China

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Recent studies have significantly increased our knowledge on Mg isotopic compositions of chondrite, the terrestrial mantle and hydrosphere. Behaviours of Mg isotopes during magmatic evolution, however, is still not well constrained. Though very limited isotope fractionation has been reported during basaltic magmatism [1], it is still unclear whether Mg isotopes can be fractionated during granite differentiation. Understanding behaviours of Mg isotopes in granites will not only shed light on Mg isotopic composition of the continental crust and global Mg isotope recycling, but also provide constrains on its petrogenesis.

Here, we reported high-precision Mg isotopic data for a set of whole-rock samples and biotite minerals from A-type Kuzigan granitoids, Xinjiang, China. The Kuzigan complex is located at the middle-east Pamir syntax and distributed along the Karakorum fault. They are LREE-enriched peralkalic syenites and syenitoids with potassium feldspar, plagioclase, biotite and aegirine-augite as their common minerals. The chemical compositions of Kuzigan complex vary widely in SiO<sub>2</sub> (54.2 to 74.8%) and MgO (0.45 to 5.50%), and enriched in K<sub>2</sub>O (K<sub>2</sub>O/Na<sub>2</sub>O>1). This complex was considered to be produced by partial melting of mafic eclogite at the base of the thickened crust during regional extension at 11Ma.

Despite the large variations in SiO<sub>2</sub> and MgO contents, Mg isotopic compositions show a very limited range at both whole-rock and mineral scales. Similar to those of terrestrial basalts, peridotites and associated olivine and pyroxenes,  $\delta^{26}$ Mg values vary from -0.39 to -0.26 for bulk granites and from -0.33 to -0.19 for biotites. The homogenous Mg isotopic composition thus suggests no significant Mg isotope fractionation occurred during magmatic differentiation within our analytical uncertainties. Consequently, our observations suggest that the thickened eclogitic lower crust has similar Mg isotopic composition to upper mantle and basalts and Mg isotopic compositions of granitoids can sample their source rocks.

[1] Teng et al. (2007) Earth Planet. Sci. Lett. 261, 84–92.

## PGE in mantle nodules from the Newer Volcanics, Victoria: Sulfide control during mantle melting

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Platinum group element (PGE) concentrations have been measured by nickel sulfide fire assay - ICPMS in a suite of 24 ultramafic nodules from volatile-rich alkaline basalts in the Newer Volcanic Province in western Victoria, Australia. Mineralogy and chemical composition of the nodules identifies them as a suite of variably melted mantle lithosphere samples ranging from highly depleted harzburgites with ~30% melt extraction to nearly unmelted 'fertile' lherzolites, from which a MORB-like melt had been extracted at depths of 40 to 45 km. This melting event produced a series of linear geochemical trends on plots of Ca, Al, Ni and Ca against MgO. Copper correlates strongly with Se, which is taken as a proxy for S, and both elements correlate strongly with Ca, implying that a sulfide component was progressively lost to the partial melt with increasing degrees of melting. However, there is no correlation of Pt and Pd (PPGE) with Se and Ca, and PPGE remain relatively constant at around 3-6 ppb each. This implies that the PGE content of the restites remained essentially constant during melting, up to the point of the most depleted harzburgite sample. This suggests that the PPGEs were retained in an 'all or nothing' manner by residual sulfide in the restite. Iridium contents show a wide and unsystematic scatter from 0.5 to 4.5 ppb, and no relationship to degree of melt extraction, implying residence of Ir in micro-nugget inclusions within silicates, although these have not been located. The petrography of the less depleted samples is complicated by the presence of veinlets of glass, interpreted as the result of flash partial melting during ascent. Element mapping using the Maia detector on the Australian Synchrotron X-ray fluorescence beamline indicates that most of the sulfides in the least depleted samples are localised as droplets within these melt veinlets, and that rare PGE minerals are associated with the sulfides. However, the volume of veinlets is far too low to account for the observed Ca-Se spread, and it appears that they have only remobilised the lowmelting intergranular component on the scale of the samples. A metsomatic origin for the sulfide-PPGE component is precluded by lack of correlation with LREE enrichment.

## Isotopic fractionation of Mo, Cu and Zn during weathering: The record from soils and rivers

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Understanding the cycling of trace metals and their isotopes between the continents and oceans is critical in order to use them as geochemical proxies to investigate palaeoclimatic processes. Dissolved Mo and Cu in rivers is isotopically heavier than the continental rocks they drain [1, 2]. It has been suggested that the retention of light Mo in soils [1] and partitioning of Cu between particulate and dissolved phases within rivers [2] are the processes responsible. The few isotope measurements of Zn in rivers so far indicate a complex system influenced by anthropogenic inputs as well as fractionation during weathering [3]. This study aims to improve our knowledge of isotopic fractionation of Mo, Cu and Zn during weathering and transport to the oceans, thereby providing a more robust foundation for the application of these isotope systems to palaeo-oceanographic questions.

We have collected river and soil samples from three soil chronosequences in Wyoming (USA), Switzerland, and Scotland. Dissolved Mo, Cu and Zn in the streams draining these young landscapes is isotopically heavy. In isotope composition vs concentration plots they define new arrays distinct from global river compilations for Mo, Cu and Zn [1, 2]. Preliminary data from sequential leaching experiments on the Scottish soils suggest Mo and Cu behaviour in soils is complex, with significant fractionation between physicochemically defined soil fractions e.g. Fe/Mn oxides and exchangeable/carbonate phases. Data collected so far also suggest, as expected from the river data, anthropogenic and weathering influences on Zn isotopic composition in soils.

These and additional data will be used to investigate the cause of isotope fractionation for Cu, Mo and Zn during the transport of these elements from the crust to the oceans.

Archer & Vance (2006) Nature Geosci. 1 597–600.
 Vance et al. (2008) EPSL 274 204–213. [3] Chen et al. (2008) Env. Sci. Tech. 42 6494–6501.

## C and N dynamics in soil microstructures: A joined STXM/NEXAFS and NanoSIMS approach

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Significant debate surrounds the question whether the abundance of certain mineral phases might serve to predict the mean residence time of soil organic matter (SOM). Several factors may contribute to the difficulties in using mineralogy as a predictor for SOM turnover. While minerals differ widely in the nature and extent of surface reactivity, long-term protection of organic molecules by sorptive interactions appears to be limited to those organic materials directly bonded to protecting mineral surfaces. A new functional view of carbon turnover dynamics in soil has gained ground over the last years. In this view, the two-dimensional concept of soil as a system composed of adsorbent (mineral surface) and adsorbate (SOM) has been extended to a three-dimensional view of soil consisting of a multitude of largely independent microstructures composed of intimate associations between microbiota and mineral building blocks.

We used a combination of scanning electron microscopy (SEM), synchrotron-based STXM/NEXAFS spectroscopy and high-resolution imaging mass spectrometry (NanoSIMS) to investigate the biogeochemical cycling of carbon and nirogen in such soil microstructures. In this contribution, we present initial results on how the incorporation of <sup>13</sup>C- and <sup>15</sup>N-labeled microbial cell residues into artificial mineral matrices and whole soils can be used to assess SOM turnover dynamics within specific microstructures.

## On the origin of kerogen

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It is widely accepted that kerogens in black shale are a necessary precursor to oil generation at oil window temperatures between 75 and 135° C. However, the presence of refractory kerogen-like materials in high P-T cosmic settings (supergiant stars near the galactic center and carbonaceous chrondrite meteorites) and terrestrial settings (mantle olivine, green schist facies black shales, hydrothermal metal deposits, and especially serpentinites), and the presence of anomalous metal content in black shale kerogen well above that found in biospheric material (elevated Ni, V, Co, Re, Os, and other PGE's) is highly anomalous to a low temperature biogenic model and requires a reconsideration of its origin as well as that of the derivative oil.

Based on an extensive literature review and our own data, we propose a new model for the origin of kerogen that is consistent with the observations above. It is suggested that most (if not all) Type 1 and Type 2 kerogens are a by-product of serpentinization (serpentine volumes are at least 10 times that of and may potentially exist under all of the planets' sedimentary basins) of two main peridotite types. Type 1 kerogen, which contains elevated nickel relative to vanadium, is probably derived from serpentinization depleted and/or lherzolite harzburgite peridotite in the upper mantle lithosphere, whereas Type 2 kerogen, which contains elevated vanadium and nickel, is derived from enriched aluminium and chrome spinel lherzolite sources. The kerogen-producing reaction occurs in greenschist and blueschist grade serpentinization 'kitchens' where kerogen is formed at highly reduced, hydrogen-nickel rich polymerization/catalytic sites under supercritical conditions.

Produced kerogen is propelled upward in the supercritical water plume until it cools below 400 °C ionizes, densifies, and reacts with hydrogen (from water breakdown) to produce two immiscible product fluids: a reductive hydrogenated, non-ionic petroleum fluid, and an oxidative bicarbonate brine component which can also contain considerable ionized halide and metal components. Only about 20% of the original kerogen material reacts to liquid hydrocarbon; the rest is carried as a refractory residium by hydrothermal brines to surface seep sites where it is exhalatively deposited as a hydrocarbon-rich chemical sediment (commonly with dolomite and metals from the bicarbonate brine component) at near-vent chemical facies of black shale sequences.

## Bulk composition of UHP metasediments and recycling of the sediment component in arc magmas via diapirs

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It is well established that a component is recycled from subducting sediments into arc magmas. This is particularly evident for Th, Be, Nd, Pb and in some cases Sr (e.g. [1, 2]). The 'efficiency' of recycling, e.g. the ratio of sediment input to magmatic output, is not well constrained. However, using sediment input and primitive magma concentrations from PLN and PLCG, or our data, plus estimates for arc magmatic flux, we find 'steady state' recycling rates are close to 100% in all arcs. If so, the residues of this process must be measurably depleted in the recycled component. Alternatively, arc magmatic fluxes have been systematically overestimated, or arc systems are far from steady state.

We have compiled and measured bulk compositions for peraluminous ultra-high pressure (UHP) metamorphic rocks. These show recycled element abundances that are almost universally indistinguishable from average shale  $\pm 1\sigma$ , except for samples with peak metamorphic temperatures, T > 1050°C, consistent with the hypothesis that trace phases retain most of the Th, Be, Pb, LREE and perhaps Sr in subducting sediments until either (a) large extents of H2O-fluxed melting or (b) dehydration-melting of phengite (e.g. [3, 4]). Strikingly, even 'fluid-mobile elements' such as U, Ba and K show no measurable depletion in peraluminous UHP rocks relative to average shale  $\pm 1\sigma$  when peak T < 1050°C. Samples with peak T > 1050°C lie at T/P higher than even the hottest estimated subduction zone geotherms.

These observations can be reconciled if subducting sediments, which are compositionally buoyant with respect to overlying peridotite, form diapirs that rise into the mantle wedge where they are heated and undergo large extents of 'super-adiabatic' decompression melting. Dynamical calculations suggest that subducting sediment layers > 200 m thick become unstable and form diapirs beneath most or all arcs worldwide. 'Grospydite' xenoliths from the mantle could be ancient residues of such a process.

Plank & Langmuir, *Nature* 1993 [2] PLN, *Chem. Geol.* PLCG. [3] Plank *et al. Nature Geosci.* 2009.
 Hermann & Rubatto, *Chem. Geol.* 2009.

## Oxygen and carbon isotope systematics during natural mineral carbonation in peridotite of the Samail Ophiolite, Oman

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We are investigating peridotite alteration in the mantle section of the Samail ophiolite in Oman. Understanding the natural system provides insights into design of enhanced, *in situ* mineral carbonation for  $CO_2$  storage, and 'negative emissions' via enhanced  $CO_2$  capture from surface waters.

Two processes are being studied: (1) ongoing, low T formation of carbonates + serpentine, and (2) fossil, higher T formation of 'listwanites' composed of carbonates + quartz. The low T system is characterized by alkaline springs (pH > 11) where Ca-OH-rich, carbon-poor waters + atmospheric CO<sub>2</sub> form large travertine terraces. The fossil system, probably active during late Cretaceous emplacement of peridotite over sediments, formed sub-surface tabular bodies up to 200 m thick that were later exposed by erosion.

Far from listwanites, 95% of 40 carbonate veins, exposed by erosion, have measurable <sup>14</sup>C with an average 'age' of ~ 25, 000 ka, just slightly older than the average 'age' for ~ 40 travertines. Thus, veins are likely part of the ongoing low T travertine system, and formed in a near-surface horizon that erodes away approximately as fast as it forms, consistent with precipitation of carbonates + serpentine from Mg-HCO<sub>3</sub> rich groundwater to form alkaline spring waters (e.g. [1, 2]). By mass balance, there are 5 to 15 kg carbonate veins per kg of travertine [3].

d<sup>18</sup>O carbonate-water exchange thermometry, using  $\delta^{18}$ O from water in Oman peridotites, yields temperatures of ~ 30-60°C for veins away from listwanite, and up to ~ 170°C for listwanite, broadly consistent with preliminary clumped isotope data on carbonates from the same samples, and with trapping of fluid inclusions at ~ 220°C in Canadian listwanites (e.g. Hansen *et al.* Can Min 2005).

Travertines with <sup>14</sup>C ages < 1 ka show correlated  $\delta^{18}$ O (30 to 15 ‰ SMOW) and  $\delta^{13}$ C (-5 to -25 ‰ VPDB) while older travertines show a small range at the heavy end of this spectrum. Biological or kinetic factors may be responsible for the fractionation in young travertines. This range may be reduced by later recrystallization or filling of porosity.

[1] Barnes & O'Neil *GSA Bull* 1969. [2] Bruni *et al. Appl. Geochem.* 2002. [3] Kelemen & Matter *PNAS* 2008

## Chemical weathering and chemical denudation as functions of ecosystem development: Mesoscale experiments

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Chemical weathering and chemical denudation are key processes controlling hydrosphere and atmosphere chemistry, as well as C partitioning in ecosystems. There is great interest in the effects of plants on the rates of these processes [1]. We hypothesize that both the rates and mechanisms of plantdriven weathering (and associated denudation) vary, depending on geologic setting and ecosystem phase. Studies of weathering and denudation in 'sandbox' experimental ecosystems [2] showed that initially, pine-driven weathering was 5X the rate of denudation, and twice the rate of weathering and denudation in a reference system with no vascular plants (Figure). After the first 5 yrs, pine-system denudation rates fell even lower, while weathering rates were not different from zero; denudation rates then trebled when aboveground biomass was harvested, consistent with previous watershed-scale experiments [3]. These results and SEM images of pine root systems lead to our hypothesis that the growing trees were adapted to the nutrient-poor experimental conditions via development of mycorrhizospheric biofilms, that attach the root system to mineral surfaces, serving both as symbiotic-microbial habitat and weathering reactor, and efficiently micro-localizing the biology, chemistry, and hydrology of weathering and nutrient uptake at the rootmicrobe-mineral interface. The harvest disturbance would have starved the biofilms and permitted cation loss by leaching. Such disturbance episodes may explain the relatively large long-term denudation rates attributed to weatheringefficient vascular systems in the Phanerozoic.



[1] Moulton *et al.* (2000) *AJS* **300**, 539–570. [2] Balogh-Brunstad *et al.* (2008) *GBC* **22**, GB1007.

## The influence of magmatic differentiation on the oxidation state of Fe in arc magmas

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Many studies of the redox conditions recorded by arc basalts indicate that arc magmas contain a higher proportion of oxidized Fe (i.e. Fe<sup>3+</sup>/ $\Sigma$ Fe) than do basalts from mid-ocean ridge settings. Arc magmas could become oxidized through shallow differentiation processes, or instead may inherit oxidized signatures from their mantle sources. Here, we present new measurements of naturally glassy olivine-hosted melt inclusions from a single eruption of Agrigan volcano, Marianas, in order to test the effects of fractional crystallization and magmatic degassing on redox conditions. We determined Fe<sup>3+</sup>/ $\Sigma$ Fe ratios in glass inclusions using  $\mu$ -XANES [1] and couple these data with major elements and S by EMP and dissolved volatiles (H<sub>2</sub>O, CO<sub>2</sub>) by FTIR.

After correcting for post-entrapment crystallization,  $Fe^{3+}/\Sigma Fe$  ratios in the Agrigan melt inclusions (0.21-0.28) are uniformly more oxidized than normal MORB, and preserve a portion of the liquid line of descent of the magma from 5.7 to 3.2 wt.% MgO. Fractionation of olivine should increase  $Fe^{3+}/\Sigma Fe$  and decrease MgO in the melt, but the data show an overall decrease in  $Fe^{3+}/\Sigma Fe$  ratios as MgO decreases. The data trends are also inconsistent with magnetite crystallization, which would drive both  $Fe^{3+}/\Sigma Fe$  and total  $FeO^*$  down sharply. Crystallization cannot explain the extent and evolution of Fe oxidation in the Agrigan magma. Degassing is often invoked to cause redox changes in magmas, but neither  $H_2O$  nor  $CO_2$  correlate with changes in  $Fe^{3+}/\Sigma Fe$  in the Agrigan melts. Sulfur concentration, on the other hand, correlates positively with  $Fe^{3+}/\Sigma Fe$ , suggesting that S degassing may relate most closeley to the  $Fe^{3+}/\Sigma Fe$  variations in the melt. The large exchange of electrons involved with converting dissolved  $S^{2-}$  in the melt into  $SO_2(S^{4+})$  vapor may drive magma reduction during S degassing. Shallow differentiation of magmas may modify magmatic redox conditions, but these processes are not ubiquitously oxidizing, and the uniformly oxidized condition of the Agrigan magma is likely inherited from its mantle source [2].

[1] Cottrell & Kelley (2009) *Chem. Geol.* **268**, 167–179. [2] Kelley & Cottrell (2009) *Science*, **325**, 605–607.

## **Redox transformations of uranium near the mineral-microbe interface**

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The vast majority of microorganisms in the subsurface are thought to exist in a surface-adhered state. However, the region within ~10 µm of the mineral-microbe interface is a fundamental, yet poorly understood, spatial regime that exerts critical control on contaminant transformations. Reactions that occur in this region can dominate subsurface reactivity, often exerting the greatest effect on transformations of a contaminant and the biogeochemical milieu in which it resides. We have used x-ray (150 nm spatial resolution) and electron microscopy to probe the spatial distribution of uranium and its valence state on a thin film of lepidocrocite with actively respiring surface-adhered bacteria (Shewanella oneidensis MR-1 and Anearomyxobacter spp.). Results of xray microspectroscopy experiments with S. onedensis MR-1 identify U (VI) associated with the surface-adhered cells and partially reduced uranium associated with the solid phase just a few microns away from the surface-adhered cells. Preliminary results of x-ray fluorescence and optical microscopy experiments with Anaeromyxobacter spp. on lepidocrocite thin films imply respiration and growth of the organism and the chance to investigate redox transformations of uranium under a microbial physiological state different from our previous studies. The implications of these results towards understanding transformations of uranium near surface-adhered bacteria will be presented.

### Volatile subduction in serpentinites

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Serpentinites represent the main pathway for  $H_2O$  and Cl subduction. The fate of noble gases in subducted serpentinites is also fundamental to investigating mantle convection and evolution.

Antigorite-schists from Erro Tobbio (Western Alps, Italy) have atmospheric noble gas concentrations an order of magnitude higher than typical basalts and Br/Cl-I/Cl similar to marine pore fluids. Fluid inclusions formed during initial antigorite breakdown have <sup>36</sup>Ar concentrations of ~5-100 ppb;  $^{84}\text{Kr/}^{36}\text{Ar}$  plus  $^{130}\text{Xe/}^{36}\text{Ar}$  compositions from seawater up to 2-3 times seawater; and enrichments in Br and I relative to Cl. The products of final antigorite breakdown represented by chloriteharzburgites from Almirez (Betic Cordillera, Spain), have noble gas concentrations similar to gas-rich basalts and contain fluid inclusions with: ~0.8-5 ppb <sup>36</sup>Ar; <sup>84</sup>Kr/<sup>36</sup>Ar plus <sup>130</sup>Xe/<sup>36</sup>Ar values of ~4-5 times seawater; and the lowest measured Br/Cl and I/Cl values. Taken together these data suggest: the 'noble gas subduction barrier' is ~85 % efficient for Ar; the heavy noble gases are subducted preferentially; and noble gases are subducted more efficiently than halogens or water.

Noble gas subduction is decoupled from  $H_2O$  and explains the heterogeneity of heavy noble gases in the mantle. Slab devolatilisation leads to widespread 'atmospheric contamination' of noble gases in arc and back-arc basalts. Whereas, deep-subduction of atmospheric Xe>>Kr>Ar explains the low <sup>40</sup>Ar/<sup>36</sup>Ar ratios and high relative abundance of atmospheric-Xe in Ocean Island Basalts. This realisation makes it possible to correlate the heavy noble gases with subducted lithophile elements for the first time.

## Gold adsorption and reduction by non-metabolizing bacterial cells

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Bacteria can adsorb Au from solution and precipitate it as cell-bound nanoparticles, but the underlying mechanisms are poorly understood. We examined the initial interactions between aqueous Au (III)-chloride complexes and bacteria by measuring the effects of non-metabolizing cells on the speciation and distribution of Au. We conducted batch Au (III) removal experiments, measuring the kinetics and pH dependence of Au removal, and tracking valence state transformations and binding environments using x-ray absorption spectroscopy (XAS). We used Bacillus subtilis or Pseudomonas putida cells suspended in 5 ppm Au (III)-(hydroxide)-chloride, 0.1 M NaClO<sub>4</sub> solutions. Both species removed > 85% of the Au from solution after 2 h below pH 5. Above pH 5, the extent of Au removed from solution after 2 h decreased with increasing pH, with  $\leq$  10% removal of Au from solution above pH 7.5. Au removal with both bacterial species was rapid at pH 3, and slowed with increasing pH. Reversibility experiments demonstrated that once the Au was removed from solution, adjusting the pH did not resolubilize the Au. However, cysteine caused Au to desorb, suggesting that the Au was not internalized within the bacterial cells during the experiments. XAS analysis indicated that  $\ge$  95% of cell-bound Au was Au (I), adsorbed to sulfhydryl and carboxyl or amino cell wall sites, with no Cl atoms present in any of the surface complexes. Bacterial exudates alone, with no cells present, also reduced aqueous Au (III), but this reduction was slow, and does not explain the presence of Au (I) on the bacterial cell walls in our experiments.

Our results suggest that Au removal occurs as a pHdependent two-step adsorption-reduction process. The speciation of the aqueous Au and the bacterial surface controls the rate of Au removal from solution. Under low pH conditions, the cell walls are only weakly negatively charged, and aqueous Au complexes adsorb readily and rapidly, and the adsorbed Au is then reduced to Au (I) by oxidized components within the bacterial cell walls. With increasing pH, the cell wall becomes more negatively charged, slowing adsorption significantly. Both species exhibit nearly identical adsorption and reduction behavior, so it is possible that the adsorption and reduction steps that bacterial cell walls promote represent common initial steps in the formation of Au (0) nanoparticles from solution.

A506

## Defining and calibrating surface complexation models for predictive simulations of reactive transport in field applications

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It is widely understood that surface complexation models (SCM's) provide the approach to describing metal- and metalloid-ion adsorption most compatible with scientific understanding of solid-liquid interfacial reactions. In systems where solutes adsorb on materials whose surface functional groups are known, SCM's written in terms of reactions between specific surface moieties and adsorbing species to form surface complexes identified spectroscopically provide a complete thermodynamic description of adsorption over a wide range of chemical conditions. However, this level of sophistication is generally not achievable in field applications, such as contaminant transport in groundwater, because of the difficulty in identifying dominant surface complexes. Surface complexation models have been successfully applied in predictive simulations of contaminant transport by identifying the minimum number of reactions required to quantify adsorption over the field-relevant range of chemical conditions

The structure and calibration of SCM's for reactive transport applications are examined using field experiments conducted in an aquifer with variable chemical conditions. Adsoprtion properties are controlled by mineral-grain coatings dominated by aluminum-substituted goethite and illite/chlorite clays of variable composition. SCM's are defined and calibrated using laboratory experiments conducted with sitespecific materials and applied to predict results of field experiments and field-scale plume characterization studies. Accounting for variable pH and dissolved salt concentrations on adsorption is examined using a series of experiments conducted with nickel, zinc, and lead. Accounting for competitive adsorption is examined in experiments with phosphate and arsenate. Incorporating surface complexation models into complex reaction networks is examined in experiments involving denitrification coupled to iron oxidation and its impact on fate and transport of arsenic and other solutes. These and studies conducted elsewhere demonstrate that surface complexation models provide a practical approach to quantifying the impact of adsorption on transport under variable chemical conditions, as typically observed in field applications.

## Dynamics of interfacial electron transfer: Implications for biogeochemical reactions

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The redox chemistry of microbe-mineral interfaces is central to many biogeochemical processes such as microbial iron respiration. Indeed, dissimilatory metal reducing bacteria (DIRB) can use insoluble metal oxides as terminal electron acceptors for anaerobic growth. DIRB possess an electron transport chain, mostly composed of multi-heme cytochromes, which forms a pathway for transporting electrons across the cell membrane and allows for interfacial electron transfer (ET) to extracellular metal oxide minerals.

Throughout this presentation, we will use hematite  $(\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) as a model iron (III) oxide mineral. Computational techniques were applied to explore the molecular interactions between a well-defined model cytochrome and hematite surfaces and to determine the rate of elementary ET reactions. The simulations indicate that interfacial ET distances of 1 nm or less can be achieved for the purpose of oxide reduction. Moreover, the calculations strongly suggest that, although feasible, the interfacial ET step is a potential kinetic bottleneck.

One of the main outcomes of microbial iron respiration is the release of iron (II) into solution. In turn, iron (II) can interact with the iron oxide surface and undergo oxidative adsorption. Therefore, the rates of iron (II) adsorption and ET reactions between adsorbed iron (II) and surface sites were computed to shed light on the mechanisms of iron (II) oxidative adsorption. Interestingly, these calculations reveal that iron (II) oxidation from an outersphere position is a possible pathway, despite the slower kinetics of the ET step, because iron (II) adsorption as an innersphere complex requires overcoming a large energy barrier.

Finally, the injection of electrons, via either microbial respiration or iron (II) oxidative adsorption, results in the net dissolution of the iron oxide mineral. Previous computational work in our group showed that injected electrons can move through iron oxide lattices via a polaron hopping mechanism. Therefore, a kinetic Monte Carlo model was designed and implemented to explore the catalytic effect of electron injection on iron oxide dissolution. The simulations indicate that dissolution rates are enhanced due to roughening of the surface, which, in turn, is a direct consequence of the ability of electrons to move away from their initial injection point.

### Archean lithospheric mantle: Plume-arc interaction

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The 2.7 Ga Abitibi-Wawa greenstone belt provides constraints on the origin and timing of Archean lithospheric mantle. Neither subcretion stacking of ocean lithosphere nor plume-only models resolve the aparent paradox of arcdominated crust but plume residue for refractory mantle lithosphere. There are two dominant volcanic sequences tectonically imbricated in a subduction-accretion complex: komatiite-tholeiite basalt sequences erupted as ocean plateau derived from mantle plumes, and bimodal tholeiitic to calcalkaline basalts and dacites erupted as intraoceanic arcs. In the model of plume-arc interaction, a migrating arc captures thick contemporaneous plateau crust which imbricate to yield the dual volcanic sequences. At 2.7-2.68 Ga TTG, that traversed a mantle wedge, were emplaced, as were diamondiferous lamprophyres constraining the PT regime of the mantle wedge. By 2.5 Ga the bouyant refractory residue of melting in the plume coupled with the crust, timed by resetting of isotopic systems in reactivated faults [1]. Later subductionrelated metasomatism of domains of refractory mantle lithosphere reset the lithosphere to lower P values.

[1] Wyman et al. (2002) Precamb. Res, 115, 37-62.

## Subsurface transport of Pu on nanominerals: Teasing out biogeochemical controls in field environments

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The ability of colloids (< 1 micron particules) to transport strongly sorbing radionuclides, such as plutonium (Pu), has been shown in a number of seminal field studies [1, 2, 3]. Despite the recognized importance of colloid-facilitated transport, little is known about the geochemical and biochemical mechanisms controlling Pu-colloid formation and association. The major challenge in predicting the mobility and transport of plutonium (Pu) is determining the dominant biogeochemical processes that control its behavior at the water-mineral interface. The reaction chemistry of Pu (*i.e.* aqueous speciation, solubility, sorptivity, redox chemistry, and affinity for colloidal particles, both abiotic and microbiallymediated) is particularly complex.

Current research at the Nevada Test Site (NTS) has shown that the transport of Pu detected in deep groundwater with low organic carbon is associated with the inorganic colloidal fraction, specifically clays. In addition, greater than 70% of the total Pu is associated with the smallest particulates, 10-100 nm. Yet, in shallower NTS groundwater with high dissolved organic carbon, the Pu is mostly dissolved and not colloidal. In contrast, Santachi *et al.* [2] has shown that at Rocky Flats the Pu is associated with the microbial fraction of the surface water. At Hanford the vertical transport of Pu in the vadose zone appear to be mineralogically controlled. We will compare results from different biogeochemical environments at NTS to elucidate the dominant controls on transport of Pu in the subsurface.

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## Geological evidence of microbial dissolution of iron carbonate

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Many exposures of continental sandstones exhibit distinctive patterns of iron-oxide cement (IOC) and iron oxide stain (IOS). These include boxworks consisting of concentric bands of IOC as well as irregular, undulatory bands of IOC. In both cases the more friable sandstone between the bands is stained with IOS. Perhaps the most spectacular example of this type of iron-mineralization is the Kanab Wonderstone. Vertically jointed sandstone bodies in the Shinarump member of the Chinle Formation contain ca. 5% Fe<sub>2</sub>O<sub>3</sub>. Much of this iron occurs as 1 to 5 mm thick, undulatory bands of iron oxide cement (IOC) that cross-cut and obscure sedimentary structures. Iron also occurs as iron oxide stain (IOS). Between each pair of IOC bands are alternating IOS and lightly stained or unstained bands of sand grains that also cross-cut and obscure sedimentary structures. The interior-most portion of the sandstone bed may contain bleached sandstone enclosed by a band of IOC.

Siderite is abundant in the lower portion of the Chinle Formation and locally (e.g. at Temple Mountain) cements large masses of sandstone. We interpret the IOC and IOS to be produced by microbially mediated dissolution of siderite and oxidation of ferrous iron. Iron-oxidizing bacteria colonized the interface between siderite-cemented sand and porous sandstone, oxidizing iron and generating acid that caused dissolution of siderite. Aqueous ferrous iron diffused back to the biofilm where it was oxidized. The bands of IOS are the remains of self-focused reaction fronts that advanced ahead of the biofilm. These features are geological evidence of past microbial activity and evidence of microbial recycling of mineralized carbonate back into the atmosphere.

## Banded iron formations from the Eastern Desert of Egypt: A new type of ore?

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Banded iron formations (BIFs) occur in 13 localities in an area approximately 30, 000 km<sup>2</sup> within the eastern desert of Egypt. Iron ore occurs as rhythmically layered bands intercalated with volcanic arc assemblages. In most cases, the BIFs display syn-sedimentary bedding and lamination. The entire sequence is strongly deformed and regionally metamorphosed under greenschist to amphibolite facies conditions.

All deposits consist of an oxide facies with magnetite and hematite, and a silicate facies made of quartz with subordinate amounts of one or more of the minerals: chlorite, greenalite, stilpnomelane, garnet, carbonate, epidote, hornblende, or plagioclase. With the exception of the northernmost jaspilite type deposit of Hadrabia, magnetite is the predominant oxide. Major and trace element data vary from one deposit to another, the most intriguing feature being their high Fe/Si compared to Algoma and Superior types. Two types are identified: a) fresh BIFs with Fe/Si ratio < 2.3 and b) altered BIFs with Fe/Si ratio > 3.0.

The relatively small nature of individual deposits, strong variations in  $Fe_2O_3$  (t) and  $SiO_2$  and high Cr, V and Ni (for most deposits) support a volcanic exhalative origin, leading most scientists to classify them as 'Algoma type BIFs'. However, the lack of sulfides, varve – like nature of some deposits, and lack of a distinct enrichment in Co, Ni, Cu, As, and Sr are at odds with such a classification. On the other hand, their Neoproterozoic age, high Fe and P contents, and presence of diamictites intercalated with at least one of the deposits are features similar to Rapitan type BIFs.

The presence of laminations and absence of wave generated structures in most Egyptian BIFs indicate subaqueous precipitation below wave base. The formation of authegenic primary magnetite, paucity of primary sulfides and siderite suggest distal precipitation under slightly euxinic conditions in basins where S and  $CO_2$  activities are low. Accordingly, Egyptian BIFs formed in the deepest 'shelf – like' environments of fore-arc and back-arc basins.

## Geochemical characteristics of hydrothermal alteration zones in the Sarcheshmeh porphyry copper deposit, SE of Iran

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#### **Porphyry copper deposits**

The Sarcheshmeh copper mine, located in the Uromieh-Dokhtar volcanic belt, is one of the largest porphyry copper deposits in east of Iran. The ore-hosting rock comprises Eocen andesites and granodiorite  $(12\pm0.5 \text{ Ma})$ . The orebodies consisting of veinlet-disseminated mineralization with grade ranging from 0.20 to 0.60% Cu [1]. The dominant ore minerals are chalcopyrite and pyrite with lesser amount of chalcocite, sphalerite and magnetite. Gangue minerals include quartz, sericite, calcite, chlorite and biotite with minor hornblende, pyroxne, epidote and calcite.

#### **Discussion of results**

Three different alteration zones (propylitic, phyllic and argillic) have been recognized with notable differences in major and trace elements behaviour [2].

LREE's in the phyllic zone with mineral assembleges (sericite, pyrite, quartz, kaolinite) are strongly enriched in comparison with argillic facies. HREE in both zones particularly in argillic facies are strongly depleted. Also, a weak negative slope is observed in the REE pattern of the propylitic zone.

High and low field strength elements (HFSE, LFSE) are enriched and depleted in phyllic and argillic zones respectively. Geochemically speaking, major and trace elements behave highly selective in different alteration facies. Sulfur isotopic determination on pyrite, galena and chalcopyrite cluster around -1.8 to +3.6  $\delta^{34}$ S suggesting a mantle – magmatic origin for the sulphides of Sarcheshmeh porphyry copper mine.

[1] Shafiei (2001) M.Sc thesis, University of Kerman, Kerman, Iran, 380p. [2] Mehrabi (2008) M.Sc thesis, University of Isfahan, Isfahan, Iran, 140p.

## Geochemistry and petrogenesis of hornblendites in an island arc tectonic setting

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Hornblendites occur as mega enclaves in granites abutting the eastern periphery of the Neoarchean Narayanpet-Gadwal granite greenstone belt trending NNW-SSE in the eastern Dharwar craton, India. The absence of chilled margins and granitic xenoliths within the hornblendites preclude an intrusive origin for these rocks whilst tectonic juxtaposition cannot be ruled out. Their texturaly coarse grained mineralogy comprises of metamorphic magnesio-hornblende, interstitial oligoclase, relict diopside, with minor zircon, magnetite and apatite. We report new major and high-precision ICP-MS trace element data for these rocks which provides significant constraints on their petrogenesis and geodynamic evolution of the associated arc volcanics in the belt. Compositionally these rocks have consistently high MgO (~17 wt%), Mg# (~0.70) and CaO (~11 wt%), low SiO<sub>2</sub> (~47 wt%), TiO<sub>2</sub> (~0.5 wt%) and Al<sub>2</sub>O<sub>3</sub> (~8 wt%), with variable Cr (400-1000 ppm) and Ni (100-300 ppm) contents. They display coherent and fractionated chondrite normalized REE ( $La_N/Yb_N \sim 4$ ) with mild negative Eu anomalies (Eu/Eu\*~0.85). Their primitive mantle normalized spider diagram exhibits depletions in HFSE (Nb, Ta, Zr, Hf, Ti) relative to light REE. Their interelemental ratios Ti/V (~10), Ti/Sc (~55), Ti/Zr (~98), Zr/Sm (~9), are distinct and similar to rocks generated in an arc setting. Therefore, we propose that the highly magnesian nature of these rocks requires prior removal of a least fractionated olivine-pyroxene bearing cumulative phase at high pressures. The depletions observed in Zr-Hf and low Zr/Hf ~ 29 ratios coupled with heavy REE fractionation  $(Gd_N/Yb_N \sim 2.6)$  in these rocks indicates an original magmatic feature due to melting of the source rock at depth with garnet in the residual phase [1]. These hornblendites define a typical geochemical signature of subduction zone magmas, although it could also reflect crustal contamination. But, their proximal association with boninite - adakite - Nb-enriched basalt suite in the Gadwal belt [2] is consistent with a subduction zone model.

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 Manikyamba & Khanna (2007) *Gondwana Research* 11, 476–491.

## Geologic storage of carbon dioxide: Potential environmental impacts of CO<sub>2</sub>-organic interactions

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Sedimentary basins in general and deep saline aquifers in particular are being investigated as possible long-term repositories for large volumes of anthropogenic CO<sub>2</sub> to mitigate global warming and related climate changes. Results obtained from detailed chemical analyses of brine and gas samples from the Frio Brine pilot (Dayton, TX), SEACARB phase III (Cranfield, MS) and other US DOE-funded multilaboratory field tests, show mobilization of DOC, including benzene and other BTEX compounds, phenols, polycyclic aromatic hydrocarbons (PAHs) and other toxic compounds, following CO<sub>2</sub> injection. The DOC values obtained in Frio samples before CO<sub>2</sub> injection were expectedly low (1-5 mg/L), increasing during the CO<sub>2</sub> injection to 5-8 mg/L. A slug of high dissolved organics (DOC values >700 mg/L), however, was observed in samples collected several weeks after injection stopped. The concentrations of organic acid anions, BTEX and PAHs in Frio samples were low (<1 mg/L), but values of formate, acetate, and toluene were higher in high DOC samples. Results obtained to date in brine samples from Tuscaloosa Formation (Cranfield), indicate mobilization and solubility enhancement of organic compounds, in particular the alkylated PAHs, following CO<sub>2</sub> injection for EOR operations. The concern about potential contamination of overlying groundwater by leakage of CO<sub>2</sub> and/or displaced brine is warranted as high concentrations of organic acid anions (<10, 000 mg/L as acetate) and toxic organic compounds, including BTEX (up to 60 mg/L, phenols (<20 mg/L), and PAHs (up to 10 mg/L), have been reported in oilfield waters, and injected supercritical CO<sub>2</sub> is both buoyant and a good solvent for organics.

## Citric acid promoted dissolution of phosphated Fe-, Al-, Ca-based binary and ternary mineral mixtures as affected by P solid state speciation: Implications for Phosphate bioavailability

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Phosphorus is an essential plant macronutrient and also a potential water pollutant. Most soils are P deficient because phosphate minerals are sparingly soluble. Citric acid is released by plant roots and microbes in response to P deficiency and is hypothesized to be the main mechanism for solubilising P and ameliorating Al toxicity. Our goal is to investigate citric acid promoted P dissolution in ferrihydriteboehmite, ferrihydrite-calcite, and ferrihydrite-boehmiteapatite mixtures using an integrated wet chemical, spectroscopic (P-K x-ray absorption near edge structure-XANES), and microscopic (transmission electron microscopy) approach. P dissolution and release in acid and alkaline soils is mainly controlled by P sorption to Fe and Al-oxyhydroxide minerals and Fe-oxide and calcite minerals respectively. Ferrihydrite and boehmite are poorly crystalline analogs of Feand Al-oxyhydroxides respectively in soils. The current understanding of organic acid mediated phosphate dissolution is limited by the lack of a molecular scale characterization of its solid state speciation. We hypothesize that citric acid promoted phosphate dissolution in binary and ternary mixtures is controlled by its quantitative distribution between minerals. Previously, we showed using P K-XANES spectroscopy that phosphate distributed itself between ferrihydrite and boehmite essentially in proportion to its maximum sorption capacity on each mineral and more phosphate dissolved from Fe-oxide minerals. We will present results from experiments characterizing citric acid promoted phosphate dissolution in single minerals and mineral-mixtures as a function of pH (4, 6, and 8) and time to understand the role of mineral interactive effects on P dissolution in soils.

## The structural equilibria in heterogeneous silicate systems: On the hypothesis to practice

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The structural disproportionation equilibria are known in the simple silicate systems and glasses [1]. So, very likely, the simulation of phase equilibria in heterogeneous silicate systems should also include the structural melt equilibria modelling. This idea starts from the concept that increasing of some sort of structural units promotes the crystallization of corresponding crystalline phase, while the structural equilibrium guaranties rheological melt stability.

Some heterogeneous and structural equilibria, occurring in known reaction points [2], [3], are shown (Table 1).

These equilibria are sensitive to pressure. Its may be used for modeling the system behaviour in dynamics, including mineral dilution process and the fluid-melt interaction. The heterogeneous equilibria can be used for determination of the melt species thermodynamic properties

T°C	Heterogeneous and	ΔrH	ΔrG	Κ
	structural equilibria	kJ	kJ	
1558	$Fo + SiO_2 = En$	-8.94	-9.85	1.91
	$Q^0 + Q^4 = 2Q^2$			
1270	An + Ol = Di +	269	0.21	0.98
	$+ MgAl_2O_4 + SiO_2$			
	$4Q^4 + Q^0 = 2Q^2 + 2Q^4 + Q^4$			
1317	An + Ol = Sp +	149	28.5	0.12
	+ CaMgSi2O6 + SiO2			
	$Q^0 + Q^4 = 2Q^2$ (abr.)			
1232	3An+2Geh+4Ol=	-102	-2.27	1.20
	=5Di+2CaTsch.Px+3Sp			
	$Q^4 + 2Q^1 + 2Q^0 = 7Q^2$			
	(abr.)			
	An + $Na_2Si_2O_5$ + $3SiO_2$			
	$= 2Ab + CaSiO_3$			
	$2Q^3 = Q^4 + Q^2$ (abr.)			

**Table 1:** The enthalpy change  $\Delta r$ H, Gibbs function change  $\Delta r$ G and constants K of equilibria are calculated using thermodynamic data [4]. The melt species are italicized.

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## Cr-rich smectite from a natural analogue of Suweileh cementitious repository, Jordan

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A green smectite from the new cementitious natural analogue of Suweileh area, Jordan acts as a sink for heavy metals. The Cr-rich smectite is found along bedding planes in sedimentary phosphatic limestone and marl of upper Cretaceous age at a distance of a marble zone (cement zone). The mineralogy of the marble is comparable to that of cement clinker and the hydrated cement products. The original rocks were highly bituminous and similar to their stratigraphic equivalent in central Jordan that was formed by spontaneous combustion of the bituminous precursor. Most of the metamorphic rocks are massive marbles similar in composition to Portland cement. The structural formula of Suweileh smectite is calculated as follows:

The scanning electron micrographs have indicated continuous and uninterrupted smectite crystal growth. Cr-smectite was precipitated as a secondary phase in voids and fissures after the metamorphic event. The infiltration of highly alkaline water through the combusted zone has led to the leaching of  $Cr^{3+}$  ion and the precipitation of Cr-rich smectite in the marly beds of the Phosphorite Unit.

The presence of Cr-rich smectites may suggest the use of Suweileh outcrops as analogues with the repository disturbed zone. Cr-Smectite is expected to be a sink for the alteration products as radionuclides and heavy metals in the late stage evolution of a high pH plume.

## Oceanic production of organicenriched marine aerosols: Uncertainties and impacts

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Historically, the oceans have been considered an important source of supermicron aerosol mass to the atmosphere. Since these aerosols are very short-lived and largely composed of sea salt, they were previously thought to have a relatively small impact in the atmosphere. However, this paradigm is changing rapidly as new techniques and approaches to study marine aerosols are developed. Several recent studies have examined marine aerosol source functions and chemical composition, and these studies indicate that marine aerosols are dominated number-wise by submicron aerosols [1, 2] that are highly enriched in marine-derived organic matter [2, 3], representing a significant global-scale carbon flux to the atmosphere [4]. These and other published studies [5] provide strong evidence that marine aerosols, and in particular organic-rich submicron aerosols, play an important role in controlling the Earth's radiation balance, cloud formation and properties, and the chemistry of the marine atmosphere. Despite recent advances, many uncertainties remain and significant differences have been observed [5]. This presentation will highlight these advances, uncertainties and differences, with an emphasis on marine-derived organic matter present in these aerosols.

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## EPMA, FTIR and LA-ICP-MS determination of the composition of fluid microinclusions in diamonds

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The analysis of sub-micrometer fluid inclusions poses difficult analytical challenges. In the case of diamonds, most studies use EPMA to determine the bulk major element composition of sub-surface inclusions. Due to their small size, the average analytical sum (oxides + chlorine) in the inclusions is only ~6%. Still, the analysis of ~50 inclusions yields a good average composition of the fluid trapped in the diamond. Analysis of mineral micro-inclusions found in some of the diamonds indicated accuracy of ~10%.

Quantification of IR absorbance of the secondary phases that formed upon cooling of the fluid yields the absolute concentration of mica, carbonate, apatite, quartz and water in the inclusions. Combining these data with the compositions of the detected minerals yields the bulk major and volatile composition of the trapped fluids. The composition calculated via IR spectroscopy compares well with the EPMA data.

LA-ICP-MS is now used by a few laboratories for diamond analysis. Using the calibration of Rege *et al.* [1], we studied the major and trace element composition of 28 diamonds. Comparison of major elements ratios (element/Fe) obtained by EPMA and LA-ICP-MS reveals good agreement between the two methods [2]. Good correlation between the trace element abundances obtained by LA-ICP-MS [1] and INAA [3] confirms the accuracy of the trace element analysis.

Combining the EPMA and LA-ICP-MS data sets we can translate the absolute concentrations of major and trace elements in the diamonds into the composition of the trapped fluids. Together with the concentrations of water and carbonate from FTIR, the full composition of the fluids and the mineralogy of the secondary assemblage that crystallized from them are now available.

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## Noble gas isotopic compositions of zircons above the Bangombé natural fission reactor

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The Oklo-Okelobonde-Bangombé uranium deposits in the Repiblic of Gabon, are known as natural fission reactors because large-scale fission reactions occurred in the deposits 2.0 Ga ago. Significant amounts of fission products have been still remained in and around the reactors. Isotopic analysis is a useful technique to understand the behavior of fission products in and around the natural reactors. In our previous study, *in situ* isotopic analyses using a Sensitive high Resolution Ion MicroProbe (SHRIMP) showed that a part of depleted U and fissiogenic light rare earth elements were incorporated in Ubearing minerals and zircons around the Bangombé reactor [1, 2]. In this study, *in situ* isotopic analyses using a laser extraction techniques were applied for the determination of noble gas isotopic compositions in fine zircon grains from the clay layer above the Bangombé reactor.

Prior to the noble gas measurement, crystallization ages, U content and crystallinity of the zircon grains were analyzed by SHRIMP, Electron Probe Micro Analyzer and Raman microscope, respectively. The U-Pb formation ages of the zircons showed 2910±22 Ma. The U contents were in a wide range (<0.01–0.11 wt.%), and the crystallinity decreased with increasing the U content. Noble gases, He, Ne, Ar, Kr and Xe, were extracted by ablating individual zircons (> 100  $\mu$ m) with a pulsed Nd:YAG laser beam, and were measured with a modified VG5400 MS-III at the University of Tokyo.

High <sup>3</sup>He/<sup>4</sup>He ratios in all zircons suggest the production of <sup>3</sup>He by <sup>6</sup>Li (n,  $\alpha$ )<sup>3</sup>H reaction. <sup>20</sup>Ne/<sup>22</sup>Ne and <sup>21</sup>Ne/<sup>22</sup>Ne ratios in low-cristallinity grains showed significantly high values. Moreover, <sup>38</sup>Ar/<sup>36</sup>Ar ratios in low-crystalinity zircons were higher than those in high-crystalinity zircons. The results suggest the significant occurence of alpha reactions for the production of <sup>21</sup>Ne, <sup>22</sup>Ne, <sup>38</sup>Ar in low-crystallinity zircons because of the high-U contents. On the other hand, in high crystallinity zircons, neutron capture reactions predominantly occurred rather than alpha reaction, and produced <sup>36</sup>Ar. The Kr and Xe isotopic anomalies provided clear evidence for the addition of <sup>238</sup>U spontaneous-fission fragments.

[1] Hidaka *et al.* (2005) *GCA* **69**, 685–694. [2] Kikuchi *et al.* (2007) *GCA* **71**, 4716–4726.

## Lithium isotopic fractionation in the spinel lherzolite xenoliths from Boeun, Korea

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Spinel lherzolite xenoliths with protogranular to porphyroclastic textures from Boeun, Korea, were enclosed in Miocene alkali basalt. Lithium concentration and isotopic compositions of olivine, clinopyroxene, and orthopyroxene separates from the spinel lherzolite, as well as those of wholerocks of the spinel lherzolites and alkali basalt, were determined by ICPMS and MC-ICPMS, respectively, after the column procedures.

The olivines, orthopyroxenes, and clinopyroxenes in the metasomatised spinel lherzolites are enriched in lithium concentrations, whereas those in unmetasomatised spinel lherzolites are depleted in lithium concentration.

The lithium isotopic compositions ( $\delta^7$ Li) of olivines (-5.4 to +3.5 ‰), orthopyroxenes (-11.4 to -0.1 ‰), and clinopyroxenes (-14.4 to -4.7 ‰) ranged far beyond the normal mantle (+4 ± 2 ‰).

The larger variations of  $\delta^7 \text{Li}$  and  $\Delta^7 \text{Li}_{\text{olivine-Cpx}}$  (5.7 to 15.7 %) with the La, Yb,  $\text{Al}_2\text{O}_3$ , and MgO contents of clinopyroxenes indicate that the partial melting and mantle metasomatism under the mantle condition and surface contamination did not affect the lithium isotopic fractionation. In addition, the lithium isotopic fractionation during transport from mantle to surface did not happen because of the texture and homogenous chemical compositions of the minerals in the spinel lherzolites. Large variations of lithium isotope compositions between the minerals may be caused due to the different lithium isotope diffusion velocity after eruption by cooling.

### Nanoparticles in biosolid products as revealed by electron microcopy

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The production and use of engineered nanoparticles has been rapidly increasing for the past few years. As of 2009, the Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars had made an inventory of more than 1, 000 consumer products that claim to have some forms of engineered nanoparticles. Engineered nanoparticles in consumer products are expected to be released into wastewater streams to a degree during and/or after the lifetime of the products, which in turn may raise concerns about their potentially adverse impact on the environment.

Biosolid materials are the byproducts of processes that clean our wastewater before the cleaned water is discharged into the aquatic environment. During these proceeses, nanoparticles may be incorporated into the biosolid matrix through aggregation and/or sorption reactions. Because nanoparticles concentrated in the biosolids may be redistributed into other environmental components, for example, through land application, incinertation or landfilling, it is very important to investigate the nature of nanoparticles in biosolid materials to assess their potential risk.

In the present study, we employed transmission electron microscopy (TEM) and scanning TEM (STEM) combined with energy dispersive X-ray specroscopy (EDX) for direct visulaization and characterization of nanoparticles in biosolid samples with sub-nanometer resolution. We successfully identified nano-sized Si and Al oxides, Ti oxides, and Ag and Zn nanoparticles in the biosolid samples with detailed analyses including the size, morphology, elemental compositions, and degree of crystallinity and aggregation. The results of our work clearly show the presence of nanoparticles in biosolid products with a great degree of heterogenity and complexity. This study will help us to evaluate further risks when these biosolid products reenter the environment.

## (Micro)spectroscopic investigations of arsenic speciation trends in mine wastes

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Extensive gold and silver mining has left a legacy of contaminated mine wastes across the state of California, where large volumes of mine tailings and waste rock contain highly elevated concentrations of naturally-occurring arsenic. Characterizing trends in arsenic speciation as a function of particle size can provide insight into the processes that control arsenic transport from mine-impacted sites.

Bulk mine waste samples from the Randsburg Historic Mining District in Southern California were collected and weighed prior to dry sieving to generate 11 size range-specific fractions (from >2830 um down to <20 um). Each fraction was weighed and analyzed using ICP-AES for concentrations of 48 separate elements including arsenic, iron, and other potentially toxic metals. Micro- and bulk spectroscopic methods were then applied to selected size fractions of mine wastes, utilizing X-ray fluorescence and X-ray absorption spectroscopy (XAS) to assess the speciation, distribution, and correlation of metals of interest. Finally, the availability of arsenic from mine wastes through exposure to water or passive ingestion or inhalation was examined by leach extractions using water, a simulated gastric fluid (SGF), and a simulated lung fluid (SLF), with spectroscopic studies conducted on selected samples before and after the extractions to assess potential changes in speciation.

Results show that arsenic is typically more concentrated in the finer grain size fractions, often by over an order of magnitude, potentially increasing its mobility, reactivity, and bioavailability. A mixture of arsenic-bearing species were identified by micro- and bulk XAS in most size fractions, including the presence of phases including scorodite (FeAsO<sub>4</sub>), arseniosiderite (Ca<sub>2</sub>Fe<sub>3</sub> [O<sub>2</sub> (AsO<sub>4</sub>)<sub>3</sub>]•3H<sub>2</sub>O), and As (V) sorbed to ferrihydrite. Slight changes in arsenic speciation with particle size correspond to the removal of more soluble crystalline phases and the formation of sorbed arsenic species (i.e. to iron oxyhydroxides), which may partially offset the potential toxicity of arsenic in fine-grained fractions. However, SGF studies show that under acidic conditions arsenic is still preferentially released in the finer fractions, even when corrected for surface area effects, and that more soluble arsenic phases can be shown to be preferentially removed during SGF extractions.

## Investigation of microbial calcification in Laduk spring, Yellow Stone National Park by TEM

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To understand the mechanism of calcification associated with microbial activity in hot spring, the evolution of calcite formation in Laduk spring, Yellow Stone National Park was investigated by scanning and transmission electron microscopy (SEM/TEM), as well as prelimina optical microscopy (OM). Focused Ion Beam (FIB) technology was applied to prepare the TEM samples providing homogeneous phase of calcite. The samples with various degree of calcification such as microbial mat dominant phase, mixture phase of microbial mat and calcite minerals, and multi-layered calcite dominant phase were collected from a single hot spring. Each sample may represent the stage of calcification associated with microbial activity. OM and SEM observations indicated that the morphology of calcite evolves from aggregates of round-shaped calcite to long and multi-layered calcite surrounded by biomass (Fig. 1). The nano structure of calcite was analyzed by TEM. The selected area electron diffraction (SAED) patterns showed c-reflections indicating superstructures (Fig. 2). The preliminary results in this study indicated that the calcite precipitates randomly mixed with biomass at the initial stage of calcification may grow forming a layered calcite inside the biomass. The growth of layered calcite may be promoted by the biomass resulted from microbial activity. These results were supported by the spatial relationship between calcite precipitates and biomass and the fraction of C-isotope of calcite precipitates. X-ray microanalysis on calcite precipitates detected only sulfur as impurity element. Superstructures in calcite induced by the random substitution of cations such as Mg<sup>2+</sup>, Fe<sup>2+</sup>, and Mn<sup>2+</sup> in calcite was reported in Reksten (1990 Am. Miner. 75, 807). More TEM investigation is required to understand the origin of superstructures in calcite.



Figure 1: A. OM micrograph of multi-layered calcite inside the biomass. B. SAED pattern of calcite showing c-reflections.

## Identification of natural versus anthropogenic contributions to groundwater geochemistry using an integrated hydrochemical, statistical, and mass balance modeling approach

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For hydrochemistry data from 365 samples of surface water and groundwater (alluvial, bedrock, and deep thermal groundwaters) from 150 sites in the Pocheon area, South Korea, a combined hydrochemical, environmental isotopic, statistical, and mass balance modeling approach was used to assess the relative contributions of natural versus anthropogenic sources and processes. The hydrochemistry of groundwaters was highly variable with the concentrations of NO<sub>3</sub><sup>-</sup> (mean 27.3 ± 24.0 mg/L), Cl<sup>-</sup> (mean 28.4 ± 40.0 mg/L) and SO<sub>4</sub><sup>2-</sup> (mean 22.4 ± 27.9 mg/L) showing characteristic spatio-temporal changes. The isotopic composition of nitrate ( $\delta^{15}N = 10.8 \pm 3.9\%$  and  $\delta^{18}O = 7.4 \pm 3.4\%$ ) indicated that elevated nitrate concentrations largely originate from manure and septic effluents from villages and agricultural land use.

Fuzzy clustering yielded two subgroups of groundwater, in addition to surface water (Ca-Na-Cl-SO<sub>4</sub> type) and deep thermal groundwater (Na-Ca-HCO<sub>3</sub> type). These are: 1) a 'natural' group (Ca-HCO<sub>3</sub> type) and 2) an 'anthropogenic' group (Ca-Cl-SO<sub>4</sub>-NO<sub>3</sub> type). Projection of the four groups onto an euclidian space (i.e. principal component space) indicated three major processes controlling the hydrochemical evolution. A mixing and mass balance model (M3) based on the principal component space was finally used for a quantitative estimation of the evolution of groundwater geochemistry. Major evolution paths found were: 1) waterrock interaction involving variable mass transfers through plagioclase dissolution, calcite precipiation and cation exchange, 2) anthropogenic contamination which can be estimated using the mass difference of the sum of chloride, sulfate and nitrate from Ca-HCO<sub>3</sub> type and Ca-Cl-SO<sub>4</sub>-NO<sub>3</sub> type waters, and 3) nitrate loss via denitrification during groundwater discharge into surface water.

## Temperature dependence of <sup>13</sup>C-<sup>18</sup>O clumping in synthetic aragonite: Laboratory calibration

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A paleothermometer has recently been proposed, based on the abundance of the doubly-substituted  $CO_3^{2-}$  isotopologue,  ${}^{13}C^{18}O^{16}O_2^{2-}$ , in carbonate minerals [1, 2]. This carbonate 'clumped' isotope thermometer requires only the carbonate mineral to estimate its formation temperature, in contrast to the conventional carbonate-water paleothermometer which requires the oxygen isotope compositions of both the carbonate and parent water.

Given that only a limited number of calibration studies of the carbonate clumped isotope paleothermometer are currently available in the literature and, most importantly, previous calibrations of aragonite have included only biogenic specimens, we synthesized more than 30 inorganic aragonite samples under well-controlled laboratory conditions to obtain a aragonite clumped isotope paleothermometer. Subsequently, all of the inorganic aragonite samples were examined for their oxygen isotope fractionation with respect to their parent solution, for comparison with the previous calibration of the aragonite-water fractionation relationship [3]. We then examined the clumped isotope compositions of these samples through measurements of the abundance of  ${}^{13}C^{18}O^{16}O$  in CO<sub>2</sub> liberated by phosphoric acid digestion, focusing on those new samples that have  $\delta^{18}$ O values within 0.3 ‰ of the previous calibration of the oxygen isotope equilibrium [3]. Our results indicate a temperature dependence of <sup>13</sup>C-<sup>18</sup>O clumping in synthetic aragonite that agrees with that of Ghosh et al. [1] at 25 °C, but exhibits lower temperature sensitivity and departs significantly from that calibration at higher and lower tempreatures. Possible reasons for this discrepency will be discussed.

[1] Ghosh *et al.* (2006) *GCA* **70**, 1439–1456. [2] Schauble *et al.* (2006) *GCA* **70**, 2510–2529. [3] Kim *et al.* (2007) *GCA* **71**, 4704–4715.

## Effects of road salts on pore water geochemistry of lake sediments

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Salt de-icer is commonly applied to roads to promote safer motor vehicle and pedestrian travel during the winter season. The fate of millions of tons of roadsalt is of growing concern. Most prior study has focused on the effects of salt on roadside vegetation, but the influence of these salts on lake sediment geochemistry remains poorly understood. Therefore, the effects on lake sediment porewater geochemistry of two commonly used de-icers, NaCl and CaCl<sub>2</sub>, were investigated.

Intact lake sediment cores (d. i 5 cm, length 15 cm) were collected from the shoreline of Asylum Lake (Kalamazoo, MI, USA), and incubated in distilled water (control), NaCl (5 g/L) or CaCl<sub>2</sub> (5 g/L). A suite of redox sensitive species (pH, alkalinity, ammonium, Mn (II), Fe (II), sulfide, sulfate, phosphate), together with selected major (Ca, Mg, Na, K) and trace (Pb, Ni, Co, Cr) elements were analysed at 3 depths using 3 replicate cores for initial conditions and for each treatment after 30 and 60 days of incubation.

Some parameters were influenced little by the addition of NaCl or  $CaCl_2$ . Alkalinity increased steadily with incubation time, while ammonium and sulfide increased only slightly for all three treatments. Phosphate, sulfate and trace element concentrations were typically low in all samples.

pH, Fe, Mn, Mg, Na and Ca were significantly influenced by NaCl or CaCl<sub>2</sub> addition. The control pH was invariant at ~7.5-8 compared to ~7-7.5 with NaCl treatment and ~6.5 with CaCl<sub>2</sub>. Fe (II) and Mn (II) increased dramatically with time in the CaCl<sub>2</sub> incubations, suggesting stimulation of anaerobic Fe (III) and Mn (IV) respiration. NaCl treatments resulted in large increases with time in Mn (II), but not Fe (II), compared to controls. Na levels were significantly elevated relative to controls in the CaCl<sub>2</sub> treatments, while Ca increased greatly with addition of NaCl, consistent with promotion of ion exchange from salt addition. Mg concentrations were increased by ~5x in NaCl experiments, and by nearly 10x in CaCl<sub>2</sub> experiments. Furthermore, visual inspection of cores suggests that some of the differences in geochemistry may be due to differential growth of algal mats on the surface of the cores, which appeared to be enhanced by the application of CaCl<sub>2</sub>. Further study will be required to elucidate the role of these algal mats in altering the pore water geochemistry of these sediments.

## Surface characteristics of magnetite nanoparticles synthesized by metal-reducing bacteria

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Biologically induced mineralization occurs beginning with metal adsorption to extracellural polymers (EPS) dominated by proteins or cellural wall materials, followed by the nucleation of small metal hydroxide grains, and with sufficient time, the complete mineral formation. The microbially formed minerals show that their surfaces are coated with thin organic membrane and its origin is supposed from EPS and cellural materials in previous studies [1, 2]. These microbially formed minerals have benefits for biomedical applications because of reactive functional groups on the organic membrane. Therefore, the objective of this research was to examine the surface characteristics of magnetite nanoparticles synthesiszed by metal-reducing bacteria.

The metal-reducing bacteria were enriched from inter-tidal flat sediments. The mixed culture of bacteria synthesized magnetite ( $Fe_3O_4$ ) nanoparticles using akaganeite ( $\beta$ -FeOOH) as a magnetite precursor and glucose as an electron donor. Mineralogical characterization was performed by XRD and TEM-EDX anlyses. FT-IR and XPS were used for surface chemical analysis of the synthesized magnetite nanoparticles.

The magnetite nanoparticles formed by the bacteria had around 10 nm size and spherical shape. The microbially formed magnetite was coated with organics containing an abundance of reactive carboxyl groups without any chemical process for functionalizing them. The results of FT-IR and XPS analyses showed that the binding states of the organic materials were chemically stable. These microbial processes may lead to a simple preparation of functional organicmagnetite nanoparticle complexes, and they can be useful materials for medical applications such as contrast agents for magnetic resonance imaging (MRI), enzyme and protein immobilization and drug delivery systems (DDS).

[1] Warren & Ferris (1998) *Environ. Sci. & Technol.* **32**, 2331–2337. [2] Fowle & Fein (2001) *Geomicrobiol. J.* **18**, 77–91.

## Infrared and Raman shifts of calcite in the Kasuga contact aureole, southwestern Japan: An application for solvus geothermometer

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The calcite-dolomite solvus geothermometer is one of the widely used methods for the estimation of metamorphic temperature. The equilibrium Mg / (Mg+Ca) ratio of calcite (CaCO<sub>3</sub>) coexisting with dolomite (CaMg (CO<sub>3</sub>)<sub>2</sub>) increases with increasing temperature. Systematic analyses of infrared absorption (IR) and Raman bands for solid solutions between calcite and dolomite have been studied (e.g. [1, 2, 3, 4]); however, not much has been attempted for the solvus geothermometry. We applied these calibrations for wellstudied metamorphic limestones (metamorphic temperature: 400-630°C [5]) in the Cretaceous Kasuga contact aureole, southwestern Japan with using micro FT-IR and micro laser Raman spectrometer. IR and Raman bands of the v1 and v4 in calcite shift to higher wavenumbers with increase of metamorphic temperature (Fig. 1). Micro FT-IR and micro laser Raman spectrometry of calcite may be a powerful geochemical tool for calcite-dolomite solvus geothermometry.



Figure 1: IR v4 spectra variations of calcite.

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## Anaerobic metabolism in freshwater sediments as a methane source: A modelling study

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In freshwater sediments, carbon flow is controlled by microbially mediated processes such as hydrolysis, fermentation, and terminal metabolism. These processes act to break down organic matter, whose fate is dependent upon the terminal electron acceptors available in the environment. One such fate is methane (CH<sub>4</sub>) production, and freshwater wetlands have been estimated to account for ~20% of global CH<sub>4</sub> emissions. However, methane dynamics in these settings are generally not well understood. Because methane serves as a potent greenhouse gas, more detailed knowledge on the physico-chemical controls and biological processes affecting its production is needed.

In order to predict the effects of changing environmental conditions on methane production, process-based models developed from comprehensive datasets on freshwater systems are needed to help better understand benthic carbon cycling. Here, we present results from model simulations based on a detailed analysis of organic matter breakdown in sediment from the coast of Georgia, USA. This habitat represents a complex setting where intertidal dynamics and chemical and microbial processes influence anaerobic carbon metabolism. Data obtained from laboratory and field studies, including measurements of carbon dioxide and methane fluxes across the sediment surface, depth profiles of pore water and solid phase constituents, and rates of microbial processes, are used to constrain flow dynamics and to determine controls on biological processes taking place. This information is incorporated into a multi-component 1-D sediment model that takes into account physical transport and biomineralization of species involved in organic matter breakdown. For comparison, the analysis is carried out at sites with varying latitude and datasets from multiple seasons are investigated.

## Speciation of selenium by facultative bacteria in phosphate mine waste

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Facultative beta-proteobacteria present in groundwater from the Meade Peak member of the Phosphoria Formation in southeast Idaho have been shown to reduce soluble selenate Se (VI) concentrations using native carbon under saturated, micro-aerophilic to anaerobic conditions in batch reactors containing mined chert and shale. Operational waste management strategies that seek to promote such Se (VI) reduction in facilities constructed with materials must account for long term stability of reduced selenium in predicting future potential for transport within mine waste. Samples of sterile chert and shale exposed to a live consortium of groundwater bacteria, which demonstrated Se (VI) reduction in batch reactors, were studied using ion chromatography (IC), high performance liquid chromatography-inductively coupled mass spectrometry (HPLC-ICPMS), FEM-EDS (field emission electron microscopy with energy dispersive spectroscopy), synchrotron-XRD (s-XRD), and bulk X-ray adsorption near edge spectroscopy (XANES) to determine the aqueous and solid phase selenium reduction products in shale and chert lithologies. Aqueous analysis by IC and HPLC-ICPMS, suggest a two-step reduction process, with selenate transformed to selenite Se (IV), which was rapidly removed from solution as the reduction process proceeded. Solid phase analyses, using s-XRD and XANES, identified reduced mineral phases including selenite, elemental selenium, and selenide minerals. The relative abundance of minerals varied between the shale and chert, suggesting lithologically distinct reaction pathways and products.

## Reaction of Pu(III) and (V) with magnetite and mackinawite: A XANES/EXAFS investigation

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Plutonium is the major transuranium actinide in nuclear waste and a highly toxic environmental contaminant. As iron (II) minerals are ubiquitous and known to reduce a range of metal (loid)s, including As, Cr, Se, Pu and Np, through surface-mediated redox reactions, we investigated here the reactivity of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and mackinawite (FeS) towards Pu (III) and (V) using XAFS to analyse the oxidation state and molecular structure of the reaction products.

Mineral syntheses and reactions were carried out under anoxic conditions in N<sub>2</sub> or Ar glove-boxes. Fe<sub>3</sub>O<sub>4</sub> and FeS were reacted for 40 days in 0.1 M NaCl with Pu (1x10<sup>-5</sup>M) at approx. pH 8. <sup>242</sup>Pu was added as electrolytically prepared Pu (V) to Fe<sub>3</sub>O<sub>4</sub> and FeS, and as Pu (III) to Fe<sub>3</sub>O<sub>4</sub>.

The spectra obtained from tri- and pentavalent Pu reacted with magnetite are nearly identical; shell fitting yielded a Pu-O distance of 2.50 Å, indicative of Pu (III). Using Monte Carlo modeling of the EXAFS spectra (MC) [1], we were able to unequivocally identify a distinct Pu (III) surface complex wherein Pu (III) is connected via three oxygen atoms to three edge-sharing  $FeO_6$ -octahedra of the  $Fe_3O_4$  {111} face. This result is in disagreement with [2], where in the absence of spectroscopic evidence Pu (IV) had been proposed as the major oxidation state after reacting Pu (V) with magnetite under anoxic conditions. In the presence of mackinawite, Pu (V) was reduced to Pu (IV) as determined by both XANES and EXAFS shell fitting. The EXAFS spectrum closely resembles that of PuO2 solids and colloids. Our study demonstrates that under reducing conditions in geological environments both Pu (IV) and Pu (III) species may be relevant and migration as eigencolloids or adsorbed species may play an important role in controlling Pu mobility.

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## Bioavailability of polymer nanoparticle coatings

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Nanoparticle coatings, whether manufactured or natural, ultimately dictate the fate, transport, reactivity, and toxicicty of the particle [1]. In order to fully understand the behavior of nanomaterials in the environment, it is important to understand the fate of these coatings. An important question is whether or not coatings can be removed by microbial communities. To our knowledge, no one has demonstrated conclusively whether or not surface coatings *attached* to nanoparticles are bioavailable. The objective of this study was to demonstrate whether or not polymers covalently bound to nanoparticles are bioavailable.

Nanoparticle choice was critical for these experiments. We chose to design nanoparticles with covalently bound polymer surface coatings to eliminate coating desorption. We synthesised nanoparticles with a polystyrene-like core and polyethylene glycol (PEG) arms. Polyethylene glycol is biodegradable by certain bacteria whereas the cross-linked hydrophobic particle core is not bioavailable.

We isolated multiple strains of polyethylene glycol degrading bacteria from wastewater treatment sludge, including a *Sphingomonas sp.* and a *Chryseobacterium sp.* We grew these strains in cultures with either PEG or the polymer nanoparticles as the sole carbon source. Growth was comparable in both systems indicating that indeed polymer coatings on nanoparticles are available carbon sources for bacteria. This has significant implications regarding the fate of manufactured nanoparticles in the environment.

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## Geochemical monitoring and geochemical modeling of the CO2CRC Otway Project CO<sub>2</sub> storage pilot, Victoria, Australia

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Formation fluid monitoring and geochemical modeling of the CO2CRC (Cooperative Research Centre for Greenhouse Gas Technologies) Otway Project carbon storage pilot site was undertaken to understand the physical and chemical processes taking place during the injection of CO<sub>2</sub> into a depleted gas reservoir. The collection of high quality samples of the supercritical and aqueous phases was enabled using a multilevel U-tube downhole assembly. A total of 11 water samples from U-tube 2 (2041.8 m) and 26 from U-tube 3 (2046.3 m) were collected covering a period from preinjection to self-lift. The initial water chemistry data from the two U-tubes is very similar and follows the same trends for major and minor dissolved species analyzed. However, just prior to U-tube 2 self lift a change in composition is observed that is not consistent with the expected changes due to gaswater-rock interactions. The similarity in the water chemistry suggests that the initial water produced was dominated by a higher permeability zone in the upper portion of the perforated interval. Integration of the fluid compositional data with numerical modeling of the system indicates the pH is buffered by CO<sub>2</sub>-water-rock interactions both prior to and after the arrival of the CO<sub>2</sub>. Simulations of the filling of the reservoir show ferroan dolomite dissolution resulting in increases in the pH, Ca, Mg, Fe and HCO3 content. These results are consistent with the U-tube data indicating that some of the variations in the water chemistry may reflect the effects of carbonate dissolution.

## Improvement of SIMS oxygen isotope analyses on magnetite

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### **Crystal Orientation Effect in SIMS Analysis**

Magnetite is common in many rocks and useful for oxygen isotope geothermometry [1]. Accurate temperatures are often precluded by zoned or altered grains, so that in situ analysis of  $\delta^{18}$ O by SIMS promises improved temperature estimates. However, magnetites show a significant range of analytical bias ( $\geq$ 5‰) due to crystal orientation [2-3], which is caused by channeling of the primary ions and focusing of the secondary ions when the primary Cs<sup>+</sup> beam is parallel to planes of atoms in the crystal lattice [3]. In routine  $\delta^{18}O$ analysis using IMS-1280 at WiscSIMS (multicollector Faraday Cup; 10µm spot [4]), magnetite standard grains show reproducibilities of 0.4‰ (2SD) within single grains, but ~3‰ (2SD) from grain-to-grain due to crystal orientation effects [3]. Except magnetite and hematite, no other silicate, oxide and carbonate minerals have been found with measurable crystal orientation effects for  $\delta^{18}$ O [5].

#### Test Analyses with 13keV Impact Energy

In normal operating conditions (primary/secondary accelerating voltages of +10kV/-10kV), primary ion impact energy is 20keV with an incident angle of 21°. We examined the reproducibility of oxygen isotope analyses on standard magnetite grains at the lower impact energy of 13keV. Three analytical conditions were applied for primary and secondary voltages; +3kV/-10kV, +6.5kV/-6.5kV and +10kV/-3kV, corresponding to the primary ion incident angles of 14°, 21° and 26°, respectively. The best results were obtained from the +3kV/-10kV condition, showing improved grain-to-grain reproducibility of 0.8‰ (2SD). For +6.5kV/-6.5kV, the reproducibility of analyses was only moderately improved to 1.8‰ (2SD), comparable to the amount of reduction in impact energy. The +10kV/-3kV test did not improve the reproducibility. The above results indicate that the crystal orientation effect in SIMS isotope analyses depends on both impact energy and incident angle of primary ion beam. Using the optimized (+3kV/-10kV) condition, SIMS magnetitequartz thermometry can be applied to crystals as small as 10  $\mu$ m with temperature resolution better than 50° at  $\leq$ 500°C.

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## Intrinsic silica metasomatism during serpentinization

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Serpentinization of peridotite is an exceptionally diverse but unsatisfactorily understood process. To gain deeper insights into the reaction pathways of serpentinization we link the petrography and mineralogy of serpentinized peridotites from ODP Leg 209 with hydrothermal serpentinization experiments, phase petrology and geochemical modeling.

In rocks from ODP Hole 1274A hydration of olivine (Ol) generates mesh rims, which reveal a distinct in-to-out zoning from brucite (Brc,  $X_{\rm Mg}$   $\approx$  0.8) at the interface with Ol, followed by a zone of serpentine (Srp,  $X_{Mg} \approx 0.95$ ) + Brc ± magnetite (Mgt) and finally Srp and Mgt in the outermost mesh-rims. Completely serpentinized peridotites lack Brc. Hydration of orthopyroxene (Opx) produces Fe-rich Srp (X<sub>Me</sub>  $\approx 0.89 - 0.92$ ) while talc (Tlc) and Mgt are lacking. Since in a closed system the hydration of Ol and Opx would cause the formation of Srp + Brc and Srp + Tlc, respectively, the absence of Brc and Tlc is indicative of open system conditions and mass transport of SiO<sub>2</sub>, aq from an 'Opx-hydration cell' to an 'Ol-hydration cell'. Phase relations and geochemical reaction path models indicate that mass transport of SiO<sub>2</sub>, aq will be most effective below 400 °C, where the gradient in  $\mu$ SiO<sub>2</sub>, ag between both cells is steepest. At T below the quasiinvariant point of Ol, Srp and Brc, the addition of SiO<sub>2</sub>, aq from the Opx cell will destabilize Brc in favor of Srp. Fluid chemistry and petrographic analysis of solid reaction products of hydrothermal serpentinization experiments suggest that the hydration of Ol causes the metastable formation of Brc within the stability field of Srp before Srp nucleates, which is in accord with mineral zonings in mesh textures of samples from ODP Hole 1274A. Seeing that reaction pathways during serpentinization are strongly dependent on host-rock composition, temperature and fluid flux. further multidisciplinary studies of serpentinites from other abyssal geotectonic environments need to be conducted.

## Earth's accretion and differentiation

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Hf-W and U-Pb isotopic systematics can constrain the timing of Earth's core formation and accretion [e.g. 1], whilst metal-silicate partitioning experiments provide information on the conditions of core formation [e.g. 2]. Assuming com-plete metal-silicate equilibration during core formation, these geochemical observations are consistent with metal segregation in a deep magma ocean [2] and a rapid early accretion of Earth's main mass in ~10 Myr [3-5], followed by a late Moonforming giant impact that terminated Earth's accretion, either at ~30 Myr [4] or more likely at ~100 Myr after solar system formation [5, 6]. We developed a geochemical box model for metal-silicate differentiation in the growing Earth and show that the current observations are consistent with a much wider range of possibilities but still provide bounds on Earth's accretion and the conditions of core formation. The Hf-W observations do not provide tight constraints regarding the rate of Earth's accretion but do require that at least 36% of Earth's core formed in equilibrium with Earth's mantle. Siderophile element depletions in Earth's mantle are consis-tent with as little as 36% equilibration and do not require full metal-silicate equilibration. The U-Pb system is mainly affec-ted by Earth's terminal accretion and, provided Pb was parti-tioned into Earth's core, dates the last 10% of Earth's accre-tion to ~4.45 Ga, consistent with the Hf-W age of the Moon-forming impact [6]. This relatively late terminaton of core formation is difficult to reconcile with the preservation of a <sup>142</sup>Nd signature of a  $\leq$ 30 Myr differentiation of Earth's mantle because the isolation of the early enriched reservoir [7] would have to have occurred at a time when metal melts were still segregating into Earth's core. This seems implausible, such that the <sup>142</sup>Nd excess of Earth's mantle relative to chondrites [7] is more readily explained if the Earth has non-chondritic relative abundances of refractory elements [5, 8].

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## Boron speciation and isotope systematics in seawater, biological and inorganic carbonates

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The unique set of geochemical characteristics of the boron isotope system in seawater and marine biological carbonates makes it appealing for paleo-pH reconstructions. First, pH dependent equilibration of boric acid B (OH)<sub>3</sub>° and borate anion B (OH)<sub>4</sub><sup>-</sup> in seawater is accompanied by a large isotope fractionation, i.e. 27.2 ‰ [1]. Second,  $\delta^{11}$ B in marine carbonates suggests the predominant uptake of borate anion [2]. However, the recent discovery of both BO<sub>3</sub><sup>-</sup> and BO<sub>4</sub><sup>-</sup> coordinated structures in almost equal abundances in biogenic calcite and aragonite specimens [3] points to subtleties in biologically mediated boron uptake, which have yet to be clearly resolved. Added complexity comes from the vital effects on  $\delta^{11}$ B of marine calcifiers associated with a variable pH at the site of calcification, which is currently the area of active research [4].

We carried out a series of pH-controlled precipitation experiments of inorganic calcite and aragonite at 25°C in order to isolate purely abiological effects on carbonate  $\delta^{11}B$  during calcium carbonate precipitation from NaCl solutions (I~0.7) in the presence of borate species. Our preliminary results from aragonite precipitates at pH~8.7 are in excellent agreement with the  $\delta^{11}B$  value for aqueous borate predicted by 27.2 ‰ fractionation. Further experiments will focus on the investigation of boron partitioning into inorganic carbonates at lower pH ranges.

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# Advances in high pressure neutron scattering

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High pressure is a window to view matter in unusual states. In this talk I will show what neutron scattering is able to contribute to a better understanding of matter under pressures in the 0-30 GPa range. I will discuss the considerable efforts made recently by various groups to extend the capabilities of high-pressure neutron scattering, i.e. to achieve higher pressures and better data quality, and to make it available to a broad scientific community. The methods involved are all based on opposed-anvil techniques which allow sample volumes of up to 100 mm<sup>3</sup>. I will illustrate these advances on two examples covering molecular systems under high pressure investigated by methods which apply the so-called 'Paris-Edinburgh' high pressure technique: ice and solid oxygen.

In a recent studies we investigated the behaviour of glassy solutions of LiCl6H2O under pressure and discovered very unusual recrystallisation behaviour [1]. When this system is compressed a low temperatures to 4 GPa it recrystallizes at ~ 270 K into ice VII which incorporates Li and Cl into its structure. This form of 'salty ice VII' has unusual structural and dynamical properties, such as a 8% larger unit cell volume, exceptionally large displacement factors and 'plasticity', i e. a rotational dynamcis which is governed by hte diffusion of Li. This obeservations may have implications on modelling icy bodies of the outer solar system. The second example covers magnetism in solid oxygen under high pressure. Oxygen is the only elemntal molecule which carries a mangetic moment, and is hence able to show magnetic ordering in its solid form. In recent work we investigated solid oxygen up to pressures of 8 GPa and discovered a complex magnetic phase diagram in its 'orange phase', i.e.  $\delta$ -O<sub>2</sub> [2]. We demonstrate the existence of three different antiferromagnetic structures between 20 and 240 K. This example is a perfect illustration of the power of high pressure neutron scattering to study magnetism and structure simultaniously, as well their mutual interplay.

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## Comparability of commonly used met hods to study lignin degradation in de composing foliar litter

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Lignin is a major component of plant litter. Degradation of lignin is thought to be an important control of litter mass loss during late phases of litter decomposition. However, no existing method can determine the exact content of lignin in a litter sample. Commonly used methods to study lignn degradation utilize largely varying approaches and the comparability of these different methods is uncertain.

We assessed lignin degradation in 5 foliar litter types (ash, beech, maple, pine, spruce), exposed in the field for 27 months. Methods to analyse lignin in the litter were (i) <sup>13</sup>C-TMAH thermochemolysis and (ii) CuO oxidation each combined with GC/MS; (iii) determination of acid-detergent lignin (ADL) combined with near infrared spectroscopy. Furthermore, dissolved organic matter (DOM) produced during litter decomposition was examined for indicators of lignin-derived compounds by <sup>13</sup>C-TMAH GC/MS, UV absorbance at 280 nm and fluorescence spectroscopy.

First results suggested stronger lignin degradation in beech and needle than in ash and maple litter. Beech and needle litter showed less accumumation of ADL lignin and a stronger increase in Ac/Al ratios of CuO oxidation products during incubation. DOM production from beech and needle litter was increased in the later incubation period, and the DOM showed a high aromaticity and molecule complexity. These results suggest enhanced contribution of lignin degradation products to DOM, probably because of strong side chain oxidation indicated by high Ac/Al ratios. DOM properties thus seemed to reflect the degree of lignin degradation in the litter samples. In summary, the applied methods provided complementary information on differences in lignin degradation between the litter types over time. Combining methods that assess lignin in solid litter and DOM helped to better understand the fate of lignin during litter decomposition and its role in DOM production.

## Characterization of a new laser ablation xenotime U-Pb age standard

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With the *in situ* U-Pb dating of xenotime by SIMS and LA-MC-ICP-MS new possibilities of linking geochronological and petrological data have been opened up. But wide application of the method is presently hampered by the absence of any accepted xenotime standard for U-Pb dating.

Xenotime from a specific Weinsberg granite variety (type Plochwald) from the Bohemian Massif (Austria) seems to meet all recommendations to be suited as a U-Pb age standard. It shows a concordant U-Pb TIMS age of 315.9  $\pm$  0.6 Ma (2SD). No detectable age zonation and only relatively minor amounts of REE-U-Th-Pb inter- and intra-crystal zonation (c. 20 % with the exception of Eu with 70%) were found.

Analytical setup: New Wave 193 nm solid state laser ablation system with He as carrier gas, Nu Instruments HR-MC-ICP-MS, Nu Instruments DSN-100 desolvating nebulizer. The MS was setup to allow the simultaneous acquisition of the masses <sup>238</sup>U-<sup>233</sup>U-<sup>232</sup>Th-<sup>207</sup>Pb-<sup>206</sup>Pb-<sup>205</sup>Tl-204-Pb-<sup>203</sup>Tl. During analysis a 233U-Tl spike solution was added to the ablated material as a dry aerosol. Raw signal intensities are corrected for gas blank using 40 sec of signal acquisition prior to sample analysis. Power law and 205Tl/203Tl and 233U/205Tl in the spike solution are used to correct for mass bias of <sup>207</sup>Pb/<sup>206</sup>Pb and U/Pb ratios. The U/Pb elemental fractionation is corrected for using an intercept method applying linear regression. The calculated intercept values are corrected for mass discrimination using standard bracketing. 115 measurements on 15 xenotime crystals of 150 to 200 µm size were performed. Lines with 5µm spot size and 30 µm length were rastered with 5 µm/sec. Orientation of the laser raster parallel to the prominent {110} cleavage or parallel to crystal faces did not result in any age discrimination. All analyses resulted in concordant data points. On average, ages from single line analysis have 2SD precisions of 7.6%, 8.3%, and 5.7% for the 207Pb/235U, 206Pb/238U, and 207Pb/206Pb ages, respectively. The total mean age of all analyses (without rejections) is 313.4  $\pm$ 1.9 Ma (2SD).

We propose that the investigated xenotime can effectively be used as a standard for *in situ* LA U-Pb age dating with a spatial resolution as low as 5  $\mu$ m.

### Structures and dynamics of dense clathrate hydrates

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The ability to study the structures and dynamics of dense clathrate hydrates both at high pressures [1] and on samples recovered from high pressure [2] has enabled researchers to both more accurately characterize these materials. Studies provide insight in water potentials and the repulsive interactions between water and simple molecules or atomic species at high pressures where repulsive interactions dominate. Theses materilas are important in areas ranging from planetary science to energy or gas storage sources. In this study we will describe recent experimental and theoretical studies on dense clathrates and the closely related filled ice structures [3].

The methods employed include x-ray diffraction at both ambient and high pressure using synchrotron radiation sources, nuclear resonant inelastic x-ray scattering (NRIXS), and molecular dynamics simulations. The x-ray scattering studies at high pressure and on dense clathrates recovered from high pressure were carried out at the Advanced Photon Source, Argonne National Laboratory on samples prepared at the Nationnal Research Council of Canada.

Molecular dynamics simulations were performed using the SPC/E potential for water molecules and Lennard-Jones potentials for the Kr guest atoms. Analysis of the dynamics was performed using techniues described in our previous studies on calthrates [4].

The results allow characterization of the Kr guest atom dynamics in two dense forms, a hexagonal clathrate and the filled ice structure. The high quality of the NRIXS data also provides the temperature dependence of the Lamb-Mossbauer factor that provides insight into the strength of the interaction of the Kr guest atoms with the water molecules.

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## Anorogenic magmatism, mantle plume and the assembly of Late Proterozoic Malani supercontinent

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The Trans-Aravalli Block (TAB) of the NW Indian shield is characterized by the presence of plume related anorogenic, 'within plate, high heat producing Malani magmatism' (55, 000km2; 732 Ma). TAB is characterized by high heat flow, elevated basement, and low velocity anomaly indicative of plume tectonics. The magmatism is characterized by ring structures and is indicative of extensional tectonic environment in TAB. The Siwana granites are hypersolvus with high REE abundances, with little fractionation between HREE and LREE (La/Yb: 2.3) with marked Eu anomaly (Eu/Eu\*: 0.28). The Jalor granites are mainly subsolvus, with minor hypersolvus component, with lowest REE contents (La/Yb: 5) and Eu/Eu\*: 0.15. The Tusham granites fall in very restricted REE range, LREE are enriched with respect to HREE, La/Yb: 17, Eu/Eu\*: 0.44. The Jhunjhunu granites are subsolvus with slight enrichment of LREE La/Yb:9; Eu/ Eu\*: 0.25. The mineral chemistry of biotites from Jalor, Tusham and Jhunjhunu granites show iron eurichment trend (annite rich). Due to anhydrous conditions of magma, the Jalor biotites show high FeO / MgO ratios of 6.72 whereas the lower ratios of 4.08 and 3.72 are reported from Tusham and Jhunjhunu samples respectively. The biotites fall in the anorogenic field thereby confirming the anorogenic nature of the magma. The amphiboles in the alkali granites from Siwana evolve from richterite to arfvedsonite (magmatic subsolidus trend) and the pyroxenes in alkali granites evolve from helenbergite to aegirine through aegirine angite (acmite trend). In the Jalor granites the amphiboles belong to the composition of ferro-hornblende, ferroedenitic tschermakites. The zircons in Tusham granite belong to hydrothermal and late magmetic type whereas the Jalor zircons are magmatic. The high  $U_{2}$ content of Tusham granites is due to high abundance of uranium in the host rock (HHP granites).

## A summary of LA-ICP-MS for mineral deposit research at the US Geological Survey

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Methods development and research utilizing laser ablation ICP-MS has been ongoing at the United States Geological Survey since the early 1990's. This paper presents a summary of developments and contributions for mineral deposit related LA-ICP-MS research conducted at the USGS. From geochemical reference materials development such as sulfide calibration materials [1] and a large suite of geologic related reference materials to large scale studies of deposit related materials, the USGS has been well situated for LA-ICP-MS research. Recent work on trace element fingerprinting of deposits including work on magnetite [2], pyrite [3], bitumen [4, 5] and quartz as well as developments of rapid screening of ore related materials, trace element mapping of minerals and rocks and new directions in USGS reference materials development [6] are contributing to our work on mineral deposit research and resource assessments on national and global scales.

Through a combination of fundamental studies and imperical work our work has progressed from the microanalytical applications utilizing high spatial resolution (<100 micron) trace element mapping of mineral targets to new directions utilizing LA-ICP-MS as a rapid analytical tool for bulk powders. Utilizing the full array of LA systems in operation in the lab, full wavelength (193 nm, 213 nm and 266 nm) comparisons have been conducted for many minerals. New developments using complimentary analytical techniques such as electron microprobe, micro-XRF and Raman provide useful supporting and complimentary information that is especially useful prior to trace element LA mapping. A discussion of advantages and disadvantages of the complimentary techniques provides a useful guide for mineral deposit researchers interested in elemental analyses.

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## Pb-incorporation into synthetic Pb-doped zircon

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Zircon (ZrSiO<sub>4</sub>, *I*4<sub>1</sub>/*amd*, Z=4) is an important mineral for U-Pb chronology, and the mechanism for the incorporation of Pb is crucial to understanding the cause of U-Pb discordance. We have investigated Pb-doped zircon that were synthesized under a range of conditions [1]: (*i*.) wet at 900 °C at 1.5 GPa in the presence of P<sub>2</sub>O<sub>5</sub>; (*ii*.) dry at 1430 °C w/o P<sub>2</sub>O<sub>5</sub>; (*iii*.) wet at 800 °C at 1.0 GPa w/o P<sub>2</sub>O<sub>5</sub>, utilizing a high-resolution TEM (HRTEM) and a high-angle annular dark-field scanning TEM (HAADF-STEM).

TEM results reveal four different mechanisms for incorporation. Type I: Pb-rich particles,  $50 \sim 200$  nm, embedded in zircon. Most of the particles are associated with a single vesicle at the size of ~50 nm in diameters. These nanocrystallites are a Pb-oxide hydrate identified by selected area electron diffraction pattern (SAED). Some are present at the grain boundaries of polycrystalline zircon. Type II: Pb-rich phase concentrated at cleavage planes or grain boundaries but lacking euhedral form. Type III: amorphous Pb phase present as small spheres in 20 ~ 100 nm of diameters Type IV: Pb is homogeneously distributed in the lattice of zircon in <1 wt. % that can be detected by energy dispersive X-ray analysis (EDS).

The amount of  $P_2O_5$  present during synthesis affects the form of Pb in zircon. In the P-free system, Pb occurs as type I without detectable Pb in the matrix zircon. Under P-rich conditions (~1.3 wt. % in bulk [1]), Pb is present not only as type I but also as various forms from type II to type IV. Type IV only occurs when P is present, and this suggests that the charge balance mechanism is maintained by the coupled substitution  $[2P^{5_+} + Pb^{2_+}] \leftrightarrow [2Si^{4_+} + Zr^{4_+}].$ 

Our results indicate that the process of Pb incorporation in zircon depends on a unique combination of several experimental parameters: temperature,  $P_2O_5$  and  $H_2O$  contents. However it appears that the generation of type I particle is independent of temperature or the presence of  $H_2O$ .

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## Effects of Fe and Mn on stoichiometric characterization of dolomites by cell and Rietveld refinements

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Dolomite crystal lattice is subjected to change by cation substitutions through dissolution-precipitation reactions which impact on its stoichiometry (%CaCO<sub>3</sub>). These transformations have consequences on dolomite stability/reactivity during diagenesis and are key factors for the study of the limestone petroleum reservoir properties. Iron and manganese are presents in dolomite and this contribution presents an extension of an approach developped by Turpin *et al.* [1] using the X-ray diffractometry (XRD) technique coupled with cell and Rietveld refinements on dolomitized rock samples.

Core-samples were investigated from Chatelblanc 1 well, representing the stratigraphic contact of the Upper Muschelkalk and Lettenkohle Formations (Middle Triassic). The investigated sequence covers an interval about 10m thick, consisting of limestones, dolostones and evaporites.

The analytical approach concerning dolomite stoichiometry analyses was achieved in two phases by bibliographic approach and XRD measurement. First, an abacus – with crystallographic data on dolomites – was built from a comprehensive literature review. Such data comprise cell parameters related to the lattice Ca percentage of various dolomites. Then, using the dolomite cell parameters determined by cell refinement and this abacus, dolomite stoichiometry could be calculated. The presence of Mn and Fe was measured by EMP and EDX analyses and is taken into account to assess the methodology.

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## Imaging ion adsorption with total external reflection X-ray standing waves

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A long-standing challenge in understanding ion-mineral interactions is to be able to probe extended ion distributions. To this end, we report a new generalized model-independent approach that was developed for the analysis of long-period xray standing waves (XSW) data, which has sensitivity to probe extended structures at interfaces. The approach is applicable to various reflection geometries, including simple x-ray mirrors, and multi-layers, and is valid for XSW in an attenuating medium. The formalism allows direct extraction of the amplitudes and phases of the elemental structure factor from the measured long-period XSW data, leading to a fully modelindependent recovery of the elemental distribution. The method is validated by extracting the vertical 1D Ti profile for a TiO<sub>2</sub>/Si/Mo tri-layer sample on a Si substrate, using Ti-Ka fluorescence yield measured in ex situ and in situ environments.

This approach was then applied to probe ion distributions at nm-thick titania films in contact with Rb and Sr-containing solutions at pH ~10. Titration studies reveal that that these titania nanofilms (grown by atomic layer deposition on high surface area SiO<sub>2</sub> powders) exhibit significantly enhanced surface charge compared to single crystalline rutile surfaces. Additional long period XSW, X-ray fluorescence and X-ray reflectivity reveal this is expressed by a >2-fold higher total ion coverage on the nano-titania surface compared to rutile (110), and with a vertical ion distribution that is distinct from that observed on rutile.

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## Survival of benthic foraminifera (*Globobulimina turgida*) through intracellular nitrate respiration: A laboratory experiment

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Until very recently nitrate respiration has been considered a rare phenomenon in the eukaryotic empire. However, However the discovery of widespread occurrence of nitrate accumulation and denitrification among foraminifera [1] has challenged our understanding of the benthic N-cycling processes and the micro-organisms that mediate them. Foraminiferal denitrification is sustained through an intracellular nitrate pool. Thus, foraminifera actively collect and store nitrate in their cell, enabling them to maintain respiratory activities even when the desired electron acceptors  $(O_2 \text{ or } NO_3)$  are absent from the environment. This experimental laboratory study was designed to monitor the survival strategies of G. turgida under different oxygen/nitrate conditions. The survival rates were recorded together with the cellular adenosine triphosphate levels. Results to date show that G. turgida is able to survive in an oxygen-free environment over 3 months if nitrate is readily available. Under oxygen and nitrate-free conditions, however, survival rates are reduced, but foraminifera can survive up to 2 months if utilising their internal nitrate pool only.

[1] Piña-Ochoa, Høgslund, Geslin, Cedhagen, Revsbech, Nielsen, Schweizer, Jorissen, Rysgaard & Risgaard-Petersen (2010) *PNAS* **107**, 1148–1153.

## Fe(II) distribution in the Arabian Sea oxygen minimum zone and Western tropical Indian Ocean from GEOTRACES KH-09-5

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Fe is strongly enriched in the Arabian Sea Oxygen minimum zone during the SW monsoon because a substantial fraction is present as Fe (II) [1]. Dissolved Fe (II) was determined by chemiluminescense [2] in the Indian Ocean (18°N-20°S, 69°E) during the 2009 intermonsoon/NE monsoon on the first Japanese GEOTRACES cruise, to study the seasonal change of Fe (II) in the OMZ and its southernmost extent. Within the OMZ (Stn. ER5, ER6), Fe (II) maxima coincided with oxygen minima, but were 50% lower than during the SW monsoon [1]. However, Fe (II) extended over a broader depth range, suggesting net scavenging and vertical transport followed injection of remineralized Fe during the SW monsoon. Subsurface Fe (II) maxima were not detected in stations south of the OMZ. The implications for N cycling in the Arabian Sea will be discussed.



**Figure 1:** Fe(II) at Stn. ER5 (18°N), ER6 (15°N) and ER7 (10°N).

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## Geochemical and mineralogical characterization of Arsenic-contaminated soil at Chonam gold mine, South Korea

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Solubility of arsenic in the soil environment is mediated by redox reaction and by its association with other elements and solid phases in soil matrix. The objective of this study was to investigate the nature of arsenic contamination and its association with soil matrix by chemical extractions and mineralogical characterization.

This study examined arsenic-contaminated soil samples obtained from Chonam gold mine, Chonnam Province, South Korea. Three extractants including hydrogen peroxide [1], citrate and dithionite [2], and oxalate (pH 3) [3] were tested for chemical leaching of arsenic from the soil. Sedimentation method was used particle size separation of the Ascontaminated soil. And mineralogical characterizations of the particle-size separated soils were performed by SEM, TEM, EDS, and XRD analyses.

Arsenic concentration of the soils ranged from 1140 to 1688 mg/kg at the gold mine. Leaching results showed that the three extractants extracted 2.6% of the total arsenic for the Ascontaminated soils. Particle size analysis showed that soil texture of the soil was silt. Major minerals of sand and silt were muscovite, orthoclase, quartz, and vermiculite. Clay fraction was composed of kaolinite, muscovite, quartz, and vermiculite. Although As-bearing phases were not founded in clay fraction by XRD analysis, both SEM-EDS and TEM-EDS analyses showed arsenic was associated with clay minerals. These results suggest that arsenic was not mainly associated with organic matter and iron oxides. It may be adsorbed or coprecipitated with clay minerals in the soil matrix.

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## The bulk silicate Earth's W budget revised: Implications for the timing of core formation

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In the past years, new high-precision W concentration data have revealed strong fractionations of W from other highly incompatible lithophile elements (e.g. W, U, Ta) in arc rocks [3], in contrast to the traditional view [1;2] arguing for near constant W/U and W/Th ratios in most silicate reservoirs on Earth due to a similar incompatibility of these elements. The observed trace element fractionations reflect a selective enrichment of W in the sub-arc mantle via fluid-like subduction components [3]. Here we present further highprecision HFSE data for rocks from other tectonic settings (MORB, OIB), revealing a selective depletion of W in OIBs and MORBs relative to immobile HFSE (e.g. high Ta/W). The W budget in MORBs reflects cpx-controlled partial melting and cannot be explained by residual W-rich phases as claimed elsewhere [4]. Rather, the W depletion in MORBs and OIBs (high Ta/W) is complementary to the enrichment observed in arc rocks (low Ta/W). Together with estimated compositions of the continental crust, our data therefore permits an independent estimate of the Ta/W ratio of the Earth's primitive mantle. Similar to previous interpretations based on Nb/U and Ce/Pb systematics, our Ta/W data reveal a depletion of the depleted upper mantle (DM) in fluid mobile elements relative to the primitive mantle (PRIMA), including W. The abundance of W relative to other incompatible elements (i. e Ta/W, W/Th) in the depleted mantle is therefore not representative of the primitive mantle. According to our mass balance calculations, the W abundance of the Earth's primitive mantle is significantly lower (11 ppb) and the Hf-W ratio of the BSE is higher (ca. 27.6) than previously estimated (13-16 ppb and 17.6 [1;2]). This results in a younger core formation age that is typically inferred from <sup>182</sup>W abundance and the Hf/W of the silicate Earth.

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## Examining the cause of rejuvenated volcanism in Samoa

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Compared to other ocean islands like Hawaii, rejuvenated volcanism in Samoa is unusual in its duration, volume and geochemical composition. Rejuvenated lavas with relatively enriched isotopic compositions may have erupted for over 2 Ma from a single rift that extends across three islands. Rejuvenated lavas are particularly voluminous on Savai'i, where this eruptive series effectively repaved the entire island. The volume of lavas erupted during the rejuvenated stage on Savai'i constitutes an estimated 2.5% of the volcano, compared to <<1% in other ocean islands. An explanation for these observations may lie in the plate tectonic setting of the Samoan islands near the Tonga trench. Tectonic stresses were suggested to be responsible for enhancing both shield and rejuvenated-stage volcanism [1], although recent work has shown that the submarine base of the Samoan volcanoes fits a hotspot progression [2] and is thus consistent with the mantle plume hypothesis. Alternatively, combining hotspot processes with tectonic stresses may enhance rejuvenated volcanism.

Existing data on Savai'i consist of subaerial samples from the rejuvenated stage [e.g. 1, 3], while the underlying shield is exposed on the submarine flanks of the volcano, characterized by a distinct and extreme isotopic composition [4]. The transition between these stages is key in distinguishing between the different models for the cause of the rejuvenated volcanism. A trachyte cobble from a river draining a 500m deep canyon [3] currently constrains the timing of the rejuvenated stage (2 Ma). Interestingly, this rock type is typically found in Samoan shields, while its isotopic composition is indistinguishable from the rejuvenated lavas. Therefore, it seems the mantle source composition may have changed before the volcano's shield stage ended.

We obtained a new sample set from the canyon, including several deep sections within the volcano's stratigraphy. These samples are investigated for their isotopic compositions to test the interpretation of the cobble data, and to help illuminate the evolution of rejuvenated Samoan volcanism.

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## Plume-influenced melting of a twocomponent source beneath Iceland

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Combined trace element and Hf-Nd isotope data on postglacial basalts from Iceland are used to evaluate the relative importance of source heterogeneity and plumeinfluenced melting.

Tracers for degree and depth of melting are correlated, but there is no systematic relation between these parameters and the geographical distance from the inferred plume centre. Good correlations between Hf and Nd isotope compositions and trace element ratios that are sensitive to the degree of melting indicate that at least two source components are sampled systematically as a function of the degree and pressure of melting. The contribution of more enriched melts with low <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>176</sup>Hf/<sup>177</sup>Hf systematically decreases with decreasing depth and increasing extent of melting. Strong depletion in Rb, Ba, U and Th and enrichment in Nb and Ta compared to La in the most enriched samples from the Reykjanes Peninsula and Western Rift Zone constrain the enriched component to be similar to ancient recycled E-MORB.

The observed relationships between trace elements and isotope ratios can be reproduced with a polybaric melt mixing model that progressively mixes accumulated melts from a depleted MORB mantle and a recycled E-MORB with increasing extent of melting. The two components are sufficient for explaining the entire trace element and isotopic variability in Icelandic postglacial main-rift lavas if melts are extracted from a range of depths and the abundance of the enriched component is variable. In the Northern Volcanic Zone the abundance of the enriched component is small (~2%) and constant, whereas beneath the Reykjanes Peninsula and the Western Volcanic Zone it is more abundant (<10%) and more heterogeneously distributed.

The example of Iceland shows that the manner of melting and mixing partial melts from different sources during melt extraction controls the observed isotope trace element relationships in oceanic basalts and is crucial for understanding the relationship between melt and source composition.

## Exploring mass independent fractionation in aqueous phase sulfur chemistry: The contribution of magnetic isotope effects

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Archean sulfur mass-independent fractionation (S-MIF) has been widely recognized as the most reliable proxy for the rise of atmospheric oxygen. A decade after its discovery, the wide-ranging implications of sulfur-MIF have been discussed extensively although relatively little is known about the mechanisms causing sulfur-MIF in natural environments. A number of studies on gas-phase processes have started to advance our understanding of the possible involvement of the more usual suspects in this regard, however, experimental evidence has also implicated aqueous interactions as potential candidate for MIF in several isotope systems (most prominently for mercury). In order to test whether processes other than gas-phase UV photochemistry have contributed to mass-independent fractionation in the sulfur system throughout Earth's history, we investigated an experiment first reported by Step et al. regarding anomalous <sup>33</sup>S fractionation during aqueous-phase UV photolysis of phenacylphenylsulfone (PPS) as a model system for initial investigation. SF<sub>6</sub> high precision quadruple sulfur isotope analysis of the residual PPS after UV photolysis confirmed MIF for the <sup>32</sup>S-<sup>33</sup>S-<sup>34</sup>S triad but showed only small, purely mass-dependent fractionation between <sup>32</sup>S-<sup>34</sup>S-<sup>36</sup>S. The result confirms that MIF in this system is caused by the magnetic <sup>33</sup>S isotope and excludes other mechanisms such as nuclear volume effects or vibronic coupling that would produce concomitant MIF in the 32S-34S-36S triad. This provides a starting point for discussing the implications of magnetic isotope effects as a mechanism for mass-independent isotope fractionation in the chemical evolution of the sulfur cycle.

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## MagIC database: Comprehensive archiving and visualization of rock- and paleomagnetic data using web 2.0 technology

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#### **Relational Database for Rock and Paleomagnetism**

The Magnetics Information Consortium (MagIC) implements and maintains an online portal (http://earthref. org/MAGIC/) and relational database of rock and paleomagnetic data. The goal of MagIC is to archive all existing measurements and derived properties for future studies of paleomagnetic directions (inclination, declination) and intensities, and for rock magnetic experiments (hysteresis, remanence, susceptibility, anisotropy).

#### New Web 2.0 Online User Interfacing

To address this task the MagIC Online Database has undergone significant revisions in the past six months, with new features including a much more responsive Web 2.0 interface, result set filtering, integrated and asynchronous plotting and mapping, advanced saving options, and a rich personalized tabular layout. Queries can be saved for future use and can be built based on location, reference, methods applied, material type and geological age, as well as a visual FlashMap interface to browse and select locations. Users can also browse the database by data type (e.g. inclination, intensity, virtual geomagnetic pole (VGP), hysteresis, susceptibility) or by data compilation to view all contributions associated with previous databases, such as the Paleointensity Database (PINT), the Global Paleomagnetic Database (GPMDB), the Paleosecular Variation of Recent Lavas (PSVRL), or other user-defined compilations. The MagIC Database is continuously striving to enrich and promote Rockand Paleomagnetic research by providing the scientific community with the tools for retrieving and analyzing previous studies, and for organizing and collaborating on new activities.

## Development of a problem-based, service-learning environmental field geochemistry course

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Geoscience undergraduates need to develop a holistic understanding of complex environmental systems, yet there is a surprising lack of literature regarding student conceptions about such systems. For example, few studies have probed naïve conceptions of broad ideas, such as biogeochemical cycling, or more specific problems, such as eutrophication. Furthermore, most geoscience students would benefit tremendously from the cultivation of practical skills, e.g. learning to design rigorous field data collection and analysis protocols in spatially and temporally heterogeneous systems. Students also need to learn to effectively communicate scientific research results to the general public. However, traditional geoscience coursework provides little or no handson training regarding low-temperature environmental system field and laboratory methods, and few opportunities to communicate science to the general public. To address these gaps, we have developed a problem-based, service-learning undergraduate course. In the initial offering of the course, 16 students worked collaboratively to assess water quality in a local urban lake. They learned to use a range of tools (e.g. colorimetry, field probes, IC, corers, water samplers), designed their own field sampling protocols, and presented their study results to local community members in an openhouse poster presentation held in a local brewpub and via a witten 40-page report submitted to local neighborhood associations. The course was rigorously evaluated using a preinstruction experience survey, pre/post knowledge and attitude surveys, a postinstruction course evaluation, and a series of interviews with four students enrolled in the course. Students made remarkable gains on the multiple choice eutrophication knowledge survey (pretest mean 5, posttest mean 19, out of 25). Interestingly, in spite of these gains, attitude surveys indicated a slight increase in cognitive novelty, perhaps indicating that students became cognizant of significant gaps in their knowledge of complex systems as they completed their study. Analysis of the interviews suggest that students did develop more sophisticated conceptions of environmental systems as a result of this course, but that a few naive conceptions remained.

## Organic geochemical characteristics of the Aptian aged lacustrine bituminous limestone in the Kale (Gümüşhane) area, NE Turkey

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Jurassic-Lower Cretaceous aged carbonate sequence is widely exposed in the Eastern Pontides, NE Turkey. The black colored bituminous limestone of Aptian age is located in the upper part of this carbonate sequence. The bituminous limestone contains a fauna that indicate freshwater / lacustrine depositional environment. The aim of this study is to investigate the source rock potential and organic geochemical characteristics of bituminous limestone.

The bituminous limestone samples have total organic carbon (TOC) values ranging between 0.11 and 1.30 % with an average TOC value of 0.54%. The hydrogen index (HI) values of limestone samples vary between 119 and 448 mg HC/gr TOC (average HI 298). These HI values indicate that limestone contain gas- and oil-prone organic matter. Pyrolysis data indicate that the organic matter content in the bituminous limestone consists of Type II kerogen. Average  $T_{max}$  value for bituminous limestone samples is 438°C (434-44°C). The  $T_{max}$  values indicate that bituminous limestone samples contain early mature-mature organic matter.

In the gas chromatogram of bituminous limestone, nalkanes with high carbon number ( $C_{26}$ - $C_{30}$ ) are dominant. Pr/Ph ratio is 1.34 and this Pr/Ph ratio indicates that bituminous limestone deposited in suboxic environment.  $C_{29}$  is the dominant sterane in the bituminous limestone samples and the general ranking is  $C_{29}>C_{27}>C_{28}$ . The bituminous limestone samples have low  $C_{22}/C_{21}$  and higher  $C_{24}/C_{23}$  tricyclic terpane ratios. The  $C_{31}R/C_{30}$  hopane ratios for bituminous limestone is very low (<0.25). The high 22S/(22S+22R) homohopane ratios and low moretane/hopane ratios indicate that the bituminous limestone contain early mature-mature organic matter. O. KOROLEVA, V. BYKOV AND T. IVANOVA

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The germanate glasses and melts of X%Na2O\* (100-X)% GeO<sub>2</sub> (X = 0, 10, 20, 30) composition, were studied by high-temperature Raman spectroscopy. The main band near 420 cm<sup>-1</sup> corresponding to symmetric stretching vibrations of Ge-O-Ge bridges in the polymerized network, disappears with addition of the Na2O to GeO2, and a new intense peak near 530-540 cm<sup>-1</sup> appears. This band assigned to vibrations of three-membered rings from tetrahedral GeO<sub>4</sub>. A shoulder near 600 cm<sup>-1</sup> to the right side of the band is assigned to vibrations of connected GeO<sub>6</sub> octahedral units. The new band near 870 cm<sup>-1</sup> is observed in the glass spectrum with 20% Na<sub>2</sub>O content. An increase of Na<sub>2</sub>O content to 30% causes an appearance a new band near 790 cm<sup>-1</sup>. These bands are attributed to the vibrations of GeO4 with one and two nonbridging oxygen atom, respectively (by analogy with Q<sup>1</sup> and Q<sup>2</sup> units in silicate melts). The change in spectra during the glass-melt transition is a result of the conversion of germanium ions from six-fold to four-fold coordination with simultaneous formation of nonbridging oxygen atoms.

The spectra of germanosilicate glasses and melts of  $33\%M_2O'67\%SiO_2 + x\%GeO_2$  composition (x = 0, 20) are characterized by bands near 1090-1110 cm-1 and 935-955 cm<sup>-1</sup>, corresponding to vibrations of nonbridging bonds of  $Q^3 \mu Q^2$  silicate groups, respectively. A band at high frequencies about 870 cm<sup>-1</sup> at 20°C и 855 cm<sup>-1</sup> at 1100°C is assigned to vibrations of GeO4 tetrahedral with one nonbridging oxygen atom. The band near 555 cm<sup>-1</sup> is observed in the low-frequency region and corresponds to symmetrical valence vibrations of Si-O-Si (Ge) bridging bonds. A decrease of the band intense near 935-955 cm<sup>-1</sup> with addition of GeO<sub>2</sub> to Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, indicates that germanium atoms are glass-forming cations in glass and melt of this composition, and the addition of GeO<sub>2</sub> leads to an increase of a degree of polymerization. The comparison of germanosilicate glass and melt spectra shows some increase of the band intense near 935-955 cm<sup>-1</sup> at high temperature, and it corresponds to some increase of  $Q^2$ content.

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## Interaction of Hg and other metals with marine macroaggregates

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Macroaggregates (macrogels), appearing episodically in the Gulf of Trieste (northern Adriatic Sea), are formed by agglomeration of dissolved organic matter, mostly heteropolysaccharides of phytoplanktonic origin. Since macrogels are organic structures with large binding surfaces, they are thought to be important horizontal and vertical carriers of different and toxic substances. Therefore, once formed they offer a great opportunity for studying their complexation with metals. Although macrogels can persist in a marine environment for quite a long time, they are subjected photochemical and microbial degradation. to Macroaggregates, collected in the Gulf of Trieste (northern Adriatic Sea), were fractionated into matrix (water insoluble fraction) and interstitial water (water soluble colloids) using filtration and centrifugation. The colloidal fraction was subsequently ultrafiltered in a 'cascade fashion' through membranes with a nominal pore size of 30, 10 and 5 kDa and fractions were analyzed for carbohydrate,  $C_{org}$ ,  $N_{tot}$ ,  $P_{tot.}$ , metal (Hg, Ba, Cd, Co, Cr, Mn, Ni, U, V, Zn) and metaloid (Se and As) contents, and used for FTIR. The highest carbohydrate content and the lowest C/N ratio were associated with a higher molecular weight (MW) fraction (>30 kDa) suggesting that aminopolysaccharides and glycoproteins can be important constituents of this fraction. Analyses of ultrafiltrates revealed that Hg and other metals have a tendency to bind to a larger (>30 kDa) macromolecules while Se has a tendency to bind to a medium MW (10-30 kDa) macromolecules. The laboratory based degradation experiment, which included the indigenous microbial population, revealed an extensive degradation of organic matter especially in the smallest (5-10 kDa) fraction. Increasing Metal/Core. (atomic) ratios, except for As, at the end of the experiment suggest the preservation of suitable binding sites for most observed metals and metalloids in degraded products.

## Archean detrital zircon's age at the active East-volcanic zone of Kamchatka

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We present results of U-Pb isotopic and trace-element geochemical studies of detrital zircons collected in the area of Quaternary and the modern volcanic activity at the East-Volcanic Zone of the Kamchatka peninsula, Russia: Karymsky, Maly Semiachik, Central Semiachik, Uzon, Kihpinych and Krasheninnikov volcanoes located within the area of the Kronotsky National park. Pre-Quaternary volcanic or sedimentary rocks are not known in the area of sampling and there are no pre-Cretaceous rocks exposed in the Kamchatka peninsula.

The main goal of the study is to test a hypothesis of older basement rocks existence under the volcanoes in the melting area and to assess age of these source rocks. Recovered detrital zircons were studied by LA-ICP-MS technique using Element-XR ICP-MS and UP-213 laser ablation system.

Many of zircons were too young (much less than 1 Ma) to get quantitatively measurable U-Pb ages using LA-ICP-MS method, however a number of robust older age clusters were discovered. The most intriguing result is that more than a hundred zircon grains from three samples collected near the Karymskoe Lake produced a good discordia with ages 1940±50 Ma and 2980±20 Ma. Other less populated clusters are close to 330 Ma, 78 Ma and 2.4 Ma.

There is a correlation found between age and traceelement composition of the studied zircons: older zircons have higher Th/U ratios and more pronounced Eu anomaly than younger populations.

Obtained results reveal existence of the Achaean basement (ca 2980 Ma) under the East-Volcanic Zone of the Kamchatka peninsula as well as younger, particularly Cretaceous rocks that are known only within the Central Kamchatka Range.

### **Biogeochemistry of iron**

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The first data about nonbarrier iron accumulation by external layers of trees trunks bark were received by us on fluorite-beryllium deposit in Zabaikalye. Detailed researches of chemical elements distribution in cross-sections of trees trunks and in their other parts and species of plants were conducted here for the first time, the aim of which was - the system of nonbarrier-barrier accumulation of plants in relation with beryllium and companions of its deposits. Here suddenly it was established that over fluorite-beryllium ore body the average content of iron for four specimen was anomaly high. In external layer of pine trunks bark it was 4, 1 %, in subereous cones and roots - 5 %. These contents in nonbarrier bioobjects of pine were higher than in soils (2 % in horizon A, 3 % - in B and 1 % – in C). For these nonbarrier bioobjects PSC of iron were unusually high 2-2, 5. According to A.I. Perel'man (1989) iron is referred to the elements of average and weak biological capture with the coefficients of biological absorption (CBA=PSC) 0, n - 0, 0n. Minimal content of iron at the considered key point of beryllium deposit - 0, 8 % was established in bast (cambiums) of pine with the contents in twigs, needles and green cones equal to1, 2; 2, 1 and 1, 4 %. For given four barrier bioobjects PSC were received equal to 0, 4; 0, 6; 1, 0; 0, 7 considering an average iron content in soil equal to 2 % - considerably less, than its clark, which was equal approximately to 5 %. Established high PSC of iron on beryllium deposit are connected with pyrite form of iron in fluorite-beryllium ores containing to 50-70 % of fluorite. On this beryllium deposit it was established that iron like Be, F, Li, Pb, Zr, Ti, Si, Al has the highest relative concentrations in external layers of trees trunks bark in comparison with other layers of bark, noticeably (in 2, 5 - 4 times) enriches the small fraction of crushed pine and larch bark and forms its own minerals in the bark: pyrite, magnetite (?) and ilmenite. These data were completely confirmed and supplemented when biogeochemistry of iron on its deposits in Angaro-Ilimskii ore region was researched.

Iron in cross-sections of larch, pine, birch, cedar, fir tree, rowan-tree trunks turned out to be distributed in the same type. For all studied species of trees the maximal contents of iron in external layer of bark, and minimal – in internal layer of the youngest bast cells consisting mainly of dividing cambial cells were established. For all species of trees in 1, 5-2 times greater content of iron is established in 'young' sap-wood in comparison with 'old' nucleous wood in the central part of trunk. 213 studied bioobjects of plants were grouped for the first time according to their prospecting informativeness to this chemical element.

## Behavior of Eu during culture of *Paramecium sp.* with yeast cells sorbing Eu

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It is known that activity of microorganism has a great impact on migration of actinides released in the environments. Retardation by adsorption or precipitation on the cells is the most desirable function of bacteria. It is also known that protozoa, who prey smaller microorganism such as bacteria, are found in not only surface soil but also deep subsurface. However, no knowledge on the role of protozoa in the migration of actinides is available. The present paper investigated behavior of *Paramecium sp. (P. bursaria)* in media containing yeast sorbing Eu. Paramecium is a wellknown unicellular protozoa living in freshwater environments. Yeast, *Saccharomyces cerevisiae*, was used as a food source and Eu (III) was used as simulant of trivalent actinides.

After the contact of yeast cells (dry weight ca. 0.1g) with a 0.5mM Eu (III) solution (25ml, pH ca. 6), many nano-particles of Eu with phosphate formed on yeast cells. P. bursaria cells were cultured with those yeast cells in an inorganic salt solution containing no phosphate (400 ml). The Eu concentration in the aqueous phase increased up to about 1 µM soon after the introducing of yeast cells but quickly decreased to an almost constant level, less than 0.1 µM, after the second day of the culture. The amount of Eu leached into the aqueous phase was less than 0.1 % of the Eu on the yeast cells. As culture time advances, membranous precipitates formed. These menbranous precipitates contained undigested and digested yeast cells and dense membranous organic substance filling gaps between those cells. Many nanoparticles of Eu phosphate were observed on digested residue of yeast cells. These resulls suggest that Paramecium sp. do not impair actinide-mineralization action of microorganisms.

## Mechanisms of iron oxidation in the thermoacidophilic crenarchaeon *Metallosphaera yellowstonii*: Field and laboratory studies suggest possible role of novel proteins

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The oxidation of ferrous iron is catalyzed by microorganisms as an important source of electrons for energy conservation. High-temperature geothermal systems provide natural laboratories to study mechanisms controlling the rate and formation of Fe (III)-oxides across different temperatures and geochemical gradients. Metallosphaera vellowstonii str. MK1 was isolated from an acidic Fe (III)-oxide mat in YNP and is an aerobic, thermoacidophilic Sulfolobales capable of growth on Fe (II), pyrite, or elemental sulfur. Importantly, 16S rRNA gene sequences related to strain MK1 (>99%) are found in many different low-pH, Fe (III)-oxide microbial mats of YNP. Analysis of draft genome sequence from M. yellowstonii reveals 7 copies of heme copper oxygen reductases (subunit I) in a total of 5 different terminal oxidase complexes including the foxA-J gene cluster (thought to be specific for Fe oxidation), as well as a novel gene coding for a putative blue multi-copper oxidase (mco). Gene expression screens and reverse transcriptase (RT)- quantitative (q) PCR of field samples and cultures grown on either Fe (II), pyrite or elemental sulfur show that fox and mco genes are highly upexpressed when Fe (II) serves as the electron donor. Protein sequence analysis of FoxC indicates a novel lysine-lysine or lysine-arginine heme b binding domain and is likely the cytochrome component of a heterodimer complex with FoxG serving as a ferredoxin subunit. Bioinformatic analysis of mco indicates that this gene codes for a novel blue multi-copper oxidase with two plastocyanin type I copper domains; only three similar sequences were found in Genbank, and appear unique to members of the Order Sulfolobales. Our results show that these thermophilic archaea have evolved a unique electron transport mechanism involved in the oxidation of Fe (II) that is not apparently reproduced in other known prokaryotes. Moreover, other thermophilic iron oxidizing archaea in these acidic habitats appear to posses different mechanisms of Fe (II)-oxidation.

## Sedimentary phosphorus cycling along an oxygen gradient in the Arabian Sea: Insights from sequential extractions and X-ray spectroscopy

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Benthic phosphorus (P) cycling was studied along a water depth and oxygen gradient on the flanks of the Murray Ridge in the northern Arabian Sea. The transect covers sites from within to well below the oxygen minimum zone (OMZ), which is located between 150 - 1200 m. Sedimentary P speciation was determined both with sequential extractions and spectroscopy (X-ray Absorption Near Edge Structure). Elevated organic C/P ratios in sediments from within the OMZ compared to oxygenated sediments at greater water depth suggest enhanced regeneration of P from organic matter under low oxygen conditions. Porewater and sediment chemistry demonstrate a strong sink-switching from organic and Febound P to authigenic Ca-P phases in low oxygen settings within and directly below the OMZ. At oxygenated deep water sites, low pore water phosphate concentrations do not allow for formation of authigenic apatite. The results show that organic-rich sediments overlain by dysoxic bottom waters can effectively sequester P through authigenic apatite formation. Hence, these sediments can constitute an important long-term sink for P despite the enhanced recycling of P from organic matter under low-oxygen conditions. Insight into the mechanisms and dynamics of P authigenesis in low oxygen settings is of importance for an accurate understanding of the global marine P cycle.

## Mapping Mercury vulnerability of aquatic ecosystems across the contiguous United States

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About 20 years ago, researchers at a few locations across the globe discovered high levels of mercury in fish from remote settings lacking any obvious mercury source. We now know that for most locations atmospheric deposition is the dominant mercury source, and that mercury methylation is the key process that translates low mercury loading rates into relatively high bioaccumulation levels in aquatic food webs. Presently, almost all US states have advisories for elevated levels of mercury in sport fish, and as a result there is considerable public awareness and concern for this nearly ubiquitous contaminant issue. In some states, 'statewide' advisories have been issued because elevated fish mercury levels are so common, or the state has no effective way to monitor tens of thousands of lakes, reservoirs and wetlands. As such, resource managers and public health officials have limited options for informing the public on of where elevated mercury concentrations in sport fish are more likely to occur than others. This project provides, for the first time, a national map of predicted (modeled) methylmercury concentrations, which is the most toxic and bioaccumulative form of mercury in the environment. The map is the result of over two decades of research that resulted in the formulation of conceptual models of the mercury methylation process, which is strongly governed by environmental conditions - specifically hydrologic landscapes and water quality. National-scale trends are clearly apparnet from the modeling results, with the Gulf and Atlantic coastal plains, the northeast, lower Mississippi Valley, and the upper Midwest lakes region having the greatest predicted methylmercury concentrations.

### Influence of lithology on streamwater chemistry

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Twenty small catchments, each underlain by geochemically contrasting rock types, were studied in the lithologically diverse Slavkov Forest, northwestern Czech Republic. The area was not glaciated and is overlain by soil derived from the local bedrocks. The catchments have similar elevation (around 700 m asl), mean air temperature (around 6°C), precipitation (around 800 mm yr<sup>-1</sup>), atmospheric deposition, and vegetation cover, but contrasting bedrocks (Table 1). All catchments are forested by Norway spruce (Picea abies (L.) Karsten) plantations. Streams of the Slavkov Forest experienced anthropogenic acidification due to large industrial emissions of SO<sub>2</sub> [1]. Two catchments underlain by leucogranite and serpentinite are in the Czech GEOMON network of intensively studied catchments [2].

Contrasting streamwater compositions were generated mainly by differences in chemical weathering [3]. Very low pH and ANC were found in the streams draining leucogranite (Table 1). Granitic catchments exhibited low acid neutralizing ability potential. Catchments underlain by mica schists, gneisses, amphibolites and neovolcanites showed medium to high neutralizing potential. Serpentinite streamwater exhibited the highest pH, ANC and Mg concentrations and consequently extremely low Ca/Mg and K/Mg ratios.

Bedrock	Ν	Area	ANC	pН	Ca/Mg	K/Mg
Leucogranite	4	0.5	-30	4.4	4.5	1.0
Granite	3	0.7	-3	4.8	3.4	0.3
Mica schist	2	0.2	+50	5.5	2.3	0.4
Gneiss	2	0.3	+120	5.8	1.3	0.6
Amphibolite	4	0.5	+300	6.5	2.3	0.2
Neovolcanite	2	0.2	+700	6.3	4.1	0.1
Serpentinite	3	0.2	+850	7.2	0.1	0.01

**Table 1:** Mean streamwater chemistry of catchments. N = number of catchments, mean area in km<sup>2</sup>, ANC = Gran titration acid neutralizing capacity in ueq L<sup>-1</sup>, element mass ratios in g g<sup>-1</sup>.

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## Organic matter-mineral interactions with depth across a substrate age gradient in Hawai'i

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We examined the composition of organic matter and its interaction with soil minerals across a substrate age gradient in Hawai'i. Our objectives were to (1) determine the type of soil organic matter (SOM) that accumulates with depth (2) assess interactions between soil minerals and organic matter and (3) assess the possible mechanisms for SOM accumulation. Sequentially deeper soil samples were collected from 6 sites across a substrate age gradient (300y - 4.1My) of mantlederived lava. The sampling sites all have similar rainfall (2500 mm MAP), vegetation and topographic position. Samples from major diagnostic soil horizons were analyzed for <sup>15</sup>N stable isotope ratios and carbon composition using <sup>13</sup>C NMR. The crystallinity of soil minerals was assessed by comparing elemental release during sequential acid-ammonium oxalate (AAO) and citrate-bicarbonate dithionate (CBD) extractions. Across intermediate aged sites (20Ky-350Ky), we found the most isotopically enriched SOM pools accumulated in surface mineral horizons (Bh horizons) where alkyl abundance (based on NMR) was notably high. Intermediate age sites (20Ky-350Ky) contained increasing amounts of AAO-extractable minerals (e.g. short-range ordered minerals) with depth. A corresponding shift, at depth, of decreasing <sup>15</sup>N values, increasing C/N ratios and 13C NMR composition toward a carboxyl-carbonyl form was observed in association with increasing AAO-extractable mineral abundance. We conclude that alkyl-rich SOM in surface mineral soil horizons accumulated largely as a result of soil microbial transformation mechanisms and possibly from interaction with nanoscale Fe-Al-(oxy)hydroxides. At greater depth, an increasingly labile, hydrophilic (carboxyl-carbonyl rich) SOM form-likely to have originated from dissolved organic carbon (DOC) leached from upper organic soil horizons-was strongly correlated with the AAO extractable minerals. This is consistent with the formation and persistence of allophane at depth in these andic soils.

## The mechanisms of Sr ion exchange into partially niobium substituted sitinakite

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A 25% niobium substituted sitinakite was exchanged with strontium as time resolved X-ray diffraction data was collected. The structural modelling of this data by Rietveld methods [1] has lead to the determination of the atomic positions of the ions and unit cell parameters as strontium occupancy increases.

The starting material of the exchange experiment is the protonated phase,  $H_2Nb_{0.25}Ti_{0.75}SiO_7 \dot{a}1.5H_2O$ , with space group P4<sub>2</sub>/mcm [2-3]. Once strontium enters the unit cell, extra-framework H<sub>2</sub>O molecules shift to provide the necessary hydration coordination. These new positions of H<sub>2</sub>O result in a lowering of symmetry to the P-42m space group, and it is thought that the new hydrogen bonding network serves to enhance strontium ion diffusion into the channels of sitinakite. There is an expansion along the *ab* plane and contraction along *c* resulting in an overall unit cell volume expansion through the first few hours of exchange followed by a volume contraction as strontium is sequestered into the framework.



**Figure 1:** Strontium exchanged sitinakite, displayed along the c axis and the bonding arrangement of strontium with three framework oxygens and four H<sub>2</sub>O molecules.

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## Stimulated Cd uptake and accumulation in the plant *Arabidopsis halleri* by dissolution of Cd-bearing Fe(III) (hydr)oxides by Fe(III)-reducing bacteria

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Soils worldwide have been contaminated with industrial waste metals, such as cadmium, which may subsequently enter the food chain through plants. These metal contaminants can have dramatic effects on human and environmental health. Therefore, there is a need for the development of new techniques to efficiently remediate contaminated soils. In the present study, we combine phytoremediation and microbial mineral transformation to determine whether a more time- and cost-efficient removal of Cd from contaminated soils can be achieved. Anaerobic Fe (III)-reducing and microaerophilic Fe (II)-oxidizing bacteria were enriched and isolated from Cdcontaminated sites bearing natural populations of the metallophyte Cd hyperaccumulator plant Arabidopsis halleri. We are currently determining geochemical and microbial parameters in plant-microbe-soil microcosms to trace the microbial (im-)mobilization of Cd from Cd-bearing Fe (III) minerals by Fe (III)-reducing bacteria and Cd uptake by the plant Arabidopsis halleri. In particular, we determine whether Cd is made phytoavailable to the plant by the stimulation of naturally occurring Fe (III)-reducing bacteria which potentially release Cd from Fe (III) (hydr)oxides through reductive dissolution. The aqueous Cd can be taken up by the plant A. halleri and accumulates in the above ground tissue. By harvesting the plant, efficient removal of Cd from contaminated soils may be achieved.

## A confocal Raman proxy for affinities and fossilization mode of Silurian acritarchs

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The application of Raman spectroscopy to paleontology has opened a new era in microfossil analyses at the submicrometer scale. Confocal Raman spectroscopy permits investigation of fossil organic micro-objects in three dimensions without the need to extract the specimen from the surrounding rock matrix.

We applied Raman to study *in situ* Early Silurian organicwalled enigmatic microfossils, classified traditionally to an informal taxonomic group the Acritarcha. Based on the detection of internal spore-like bodies, acritarchs have been reinterpreted as vegetative cells of unicellular green algae (Chlorococcales) [1]. To verify the identity of the internal bodies as spores we used confocal Raman microscopy to examine their chemical and mineral content. Chemical maps of the spore-like bodies showed kerogen carbon mixed with ferrous-oxide (hematite) on the surfaces and quartz that fills the interiors. The presence of kerogen at the surface of the internal bodies underscores their biological origin, rather than as an artifact of the fossilization process.

The Raman spectroscopy results elucidate the complex fossilization history of the studied acritarchs. Early diagenetic mineral (ferrous-oxide and silica) precipitation played a key role in the preservation of their fragile spore-like reproductive structures.

[1] Kazmierczak & Kremer (2009) *Acta Palaeont. Polonica* **54**, 541–551.

## Mineral surface processes: Key to understanding contaminant dynamics

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Chemical and biological processes at mineral surfaces control the behavior of inorganic and organic contaminants in soil and aquatic environments. Additionally, mineral surface processes play important roles in rock weathering, secondary mineral formation, biomineralization, corrosion, and many other fields of geochemistry. Therefore, mineral surface processes have been studied extensively during the past decades, and the use of advanced experimental, spectroscopic, microscopic, and computational techniques has led to major advances in our understanding of mineral surface processes at the macroscopic to molecular-scales. However, in order to apply this detailed knowledge to modeling contaminant dynamics, several major challenges still have to be overcome. Some important areas of current and future research include: (i) The surface and pore structure and biogeochemical reactivity of nano-crystalline, and nano-porous solids, (ii) the influence of organic surface coatings, biofilms, and adsorbed natural organic matter on mineral surface processes such as adsorption, dissolution, and crystal growth, (iii) redox reactions occuring at mineral surfaces, and their influence on mineral transformations, (iv) the relationships between physical, chemical, and biological heterogeneity in soils and sediments, and (v) the influence of all these factors on contaminant speciation and spatial distribution. These complex interactions must be understood quantitatively in order to improve biogeochemical models of contaminant dynamics.

This keynote presentation will provide an overview of the state of knowledge in some of these important research areas, and highlight recent research. The discussed examples will serve to illustrate that a molecular-scale understanding of mineral surface processes is a key to understanding contaminant dynamics, but that investigations of complex interactions between multiple sorbate species, sorbents, bacteria, and/or organic matter are equally essential.

## Rapid detection and characterization of surface CO<sub>2</sub> leakage through the real-time measurement of <sup>13</sup>C signatures in CO<sub>2</sub> flux from the ground

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Surface monitoring of CO2 over geologic sequestration sites will be essential in the monitoring of sequestration projects. Surface monitoring is the only tool that can be used to detect and quantify leakage on the order of 1000 tons/year CO2. Near-surface detection and quantification is made complicated by large variations in natural background CO<sub>2</sub> fluxes from biological processes. Carbon isotopes of CO<sub>2</sub> provide an opportunity to distinguish between biogenic CO<sub>2</sub> fluxes from the ground and CO<sub>2</sub> leaking from a sequestration reservoir that has origins in a process giving it a distinct isotopic signature such as natural gas processing. Recent developments in commercially available wavelength scanned cavity ringdown spectroscopy (WS-CRDS) have made it possible to rapidly measure the <sup>13</sup>C and <sup>12</sup>C isotopic composition of CO<sub>2</sub> in a field setting. A portable WS-CRDS has been used to rapidly detect and characterize an intentional leakage of CO<sub>2</sub> from an underground pipeline at the ZERT experimental facility in Bozeman, Montana. Rapid (1 hour) surveys of the 100m x 100m site were collected and the resulting concentration and <sup>13</sup>C isotopic abundance maps permit the identification of specific leakage locations and clearly distinguish petrogenic sources of CO<sub>2</sub> from biogenic sources. The work simulates a survey that could be performed over an area of 100 km<sup>2</sup>, the scale of expected industrial sequestration operations. This provides a powerful tool for surface monitoring, combining the utilities of leak detection, characterization, and source identification with rapid deployment across large spatial scales and high spatial resolutions.

## Soil contamination and health risks associated with former smelting of Pb - Zn ores at Kabwe, Zambia

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Soil sampling was carried in the neighborhood of an old Pb-Zn smelter at Kabwe, Zambia, to discriminate natural concentrations of metals from those caused by dust fallout. Two soil horizons were sampled: contaminated topsoil and reference soil horizon taken at a depth of 80-90 cm that is obviously not affected by dust fallout. It was established that total Cd, Pb, Zn, Cu and Se contents are significantly higher in topsoil relative to subsurface soil over a large part of the explored area. Contents of lead in topsoil are as high as 4%, those of zinc attain a maximum of 6.7%, copper 0.7%, arsenic 0.06% and selenium 0.01%. Sequential extraction of topsoils revealed that most of Cd, Pb, Zn and Mn are present in exchangeable form or bound to carbonates and poorly crystalized ferric oxides regardless of the distance from the smelter. However, a large part of Cu in close neighborhood of the smleter is confined to oxidizable fraction, presumably to sulfides, whereas this metal in outlying parts of the contamination halo occurs in carbonate fraction. The majority of As and Fe were found in residual fraction. A modeling of gastric availability of lead and other metals revealed that the amount of available metals in topsoil increases in the following order: Fe  $\rightarrow$  As  $\rightarrow$  Cu  $\rightarrow$  Mn  $\rightarrow$  Co  $\rightarrow$  Zn  $\rightarrow$  Pb  $\rightarrow$ Cd. This indicates that lead and cadmium pose the greatest environmental hazard when dust particles are swallowed during eating unwashed vegetables or fruits. The amount of metals in soils available for metabolism by plants (plantavailable metals) increases as follows: Fe  $\rightarrow$  As  $\rightarrow$  Co  $\rightarrow$  Mn  $\rightarrow$  Cu  $\rightarrow$  Zn  $\rightarrow$  Pb  $\rightarrow$  Cd. The experiments undertaken showed that the addition of phosphate solutions to contaminated soils significantly reduces the amount of plantavailable lead and cadmium in polluted soils, while the plantbioavailability of zinc has not been affected by added phosphate. This work was supported by grant 774 No. 205/08/0321 of the Czech Academy of Sciences.

## Compound specific terrestrial leaf wax records from the Cicogna section (Italy) during the PETM

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Compound specific isotopic analyses of higher-plant leaf waxes are a valuable tool in understanding climatic changes associated with early Eocene hyperthermals. In this study  $\delta^{13}$ C,  $\delta$ D compositions from terrestrially derived leaf waxes (n-alkanes) and TEX86-based sea-surface temperature records from the relatively expanded Cicogna section in the Venetian Southern Alps (NE Italy) are presented.

Previous work has shown that terrestrial negative carbon isotope excursions (CIE) during the Paleocene-Eocene Thermal Maximum (PETM) are larger (~4-8‰) than CIEs observed in marine records (~1-3‰). However, preliminary nalkane  $\delta^{13}$ C data from the Cicogna section indicate an attenuated CIE of ~2-3‰. This datum contrasts with the CIE of ~4-5‰ observed in the neighboring Forada section. Considering the proximity of these two sites, it is expected that the trends and magnitude of the CIE would mirror each other. Observed differences point to the influence of local vegetation, runoff or perhaps the relative continuity of the outcrops. Additionally, trends in n-alkane  $\delta^{13}$ C at Cicogna are compared with the bulk carbonate  $\delta^{13}$ C and bulk organic  $\delta^{13}$ C datasets. This suite of data can potentially be used to isolate variability in CIE observed in terrestrial and marine realms.

[1] used higher-plant leaf waxes to reconstruct changes in the hydrological cycle at the Arctic during the PETM. Enrichment prior to the event was argued to reflect reduced rainout events during moisture transport resulting in drier midlatitudes and wetter North Pole. Preliminary  $\delta D$  results generated from the Cicogna section do not indicate obvious Denrichment (or depletion) prior to the event. This suggests that the changes in moisture transport hypothesized in [1] potentially occurred northwards of the Cicogna section. Further work is currently been conducted to generate a highresolution D/H record through the main body of the PETM in order to evaluate precipitation gradients between the Arctic and the Cicogna section during the peak warmth of the PETM.

[1] Pagani et al. (2006) Nature 442, 671-675.

## Mass independent fractionation of mercury and microbiology: Where can they intersect?

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Mercury (Hg) is a redox-sensitive trace metal. While all chemical forms of Hg are toxic, organomercurial compounds are extremely neurotoxic. Mercury has now been shown to exhibit both mass-dependent (MDF) and mass-independent fractionation (MIF) and the emerging Hg isotope systematics is showing tremendous potential with regard to shedding light on its complex biogeochemistry and could be used to decipher the relative importance of its multiple abiotic and microbial transformations that lead to accumulation of organomercurial compounds in the ecosystems (see review (1)). Based on experimental results, the high spin orbit coupling (SOC) in Hg compounds, the low likelihood of suppression of SOC during dark biochemical processes, and the nature of known enzyme-Hg and microbe-Hg interactions, it has been suggested that that the nuclear spin dependent MIF is unlikely to occur during dark microbial processes (2).

However, not all microbial interactions of Hg occur in the 'dark' and many biological processes occurring in the dark can potentially interact with photo-activated compounds. In order to reliably apply Hg stable isotope distribution to ascertain relative role of microbial activities and microbial products on Hg speciation, it is essential to establish if MIF and microbiology of Hg will ever intersect? In addition to presenting a review of the present knowledge of Hg stable isotope systematics, this paper will attempt to innumerate and explore factors that can influence the above mentioned intersection. New and old experimental strategies or theoretical calculations that could be potentially applied to better understand these factors will also be discussed.

[1] B. A. Bergquist, J. D. Blum, (2009) *Elements* **5**, 353 [2] K. Kritee, T. Barkay, J. D. Blum, (2009) *Geochim. Cosmochim. Acta* **73**, 1285.

## Carbon burial and benthic fluxes in coastal marine sediments: Model study and sensitivity analysis

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The response of calcareous coastal marine sediments to changes in ocean chemistry and productivity is not yet fully understood. The efficiency of seafloor carbon burial is nevertheless important to quantify in the context of ongoing ocean acidification. We developed a one-dimensional reactive transport model to study the effect of changes in particulate inorganic carbon (PIC) and particulate organic carbon (POC) deposition fluxes on carbon burial efficiency in coastal sediments. The model incorporates the transport processes of sediment accumulation, advection, diffusion, bioturbation and bioirrigation with reactions including the redox pathways of organic carbon oxidation, re-oxidation of reduced nitrogen, iron and sulfur compounds, acid-base chemical equilibria, and dissolution of particulate inorganic carbon (calcite, aragonite, and Mg-calcite). The following processes are also included: precipitation of iron sulfide and iron carbonate, sorption of Fe (II), ammonium and phosphate, sulfidization of organic matter, and pyritization.

Model predicted benthic fluxes of dissolved inorganic carbon (DIC) and alkalinity  $(A_T)$  are estimated to be 100 Tmol C/yr and 90 Tmol A<sub>T</sub>/yr for the global coastal ocean, respectively. These return fluxes are weakly sensitive to changes in seawater pH, but are very sensitive to Fe (III) deposition fluxes. At least 93% of the labile POC is oxidized via sulfate reduction, which is responsible for ≥57% of alkalinity generation. PIC dissolution, ammonification, and iron reduction also contribute at least 10% to net alkalinity fluxes. The effect of changes in PIC and POC depositional fluxes up to 2X present-day estimates are simulated. Mgcalcite completely dissolves in all simulations, while aragonite dissolves completely when the POC:PIC ratio is greater than 7. Calcite dissolution commences when POC:PIC is greater than 10. The reactive-transport modeling approach proposed here thus provides a means to estimate changes in the magnitude of carbon and nutrients burial and recycling fluxes as a result of changes in ocean productivity.

## Regional correlation of the Precambrian basement across the Baltic Sea (N Poland): Evidence from U-Pb dating of accessory zircon

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Accessory zircon is an extremely effective tool in deciphering the chronology and affinities of the covered Precambrian basement. One isolated drill hole close to the southern Baltic coast - Slupsk IG1, reached basement at 5095 m, and 25 m of basement core biotite gneiss was recovered. The protolith of the gneiss has been interpreted either as a sedimentary sequence, or a deformed granitoid, the age and origin of which might be analogous to the Mesoproterozoic rocks on Bornholm Island that were formed during Danopolonian orogeny. CL imaging shows that most of the zircon grains consist of a large core with simple igneous zoning surrounded by an overgrowth with little or no zoning. SHRIMP U-Pb isotopic analyses of 39 cores and 39 overgrowths have shown all to be almost the same age within analytical uncertainty, a result consistent with the rock being metaigneous. About 20% of the analyses, most with relatively high common Pb, are moderately to strongly discordant, indicating an episode of Pb isotopic exchange. With only two exceptions the analyses are co-linear, allowing the age of the event to be estimated from the lower concordia intercept, 513  $\pm$  34 Ma. The upper intercept, and the mean radiogenic <sup>207</sup>Pb/<sup>206</sup>Pb of the most concordant data, give estimates of the crystallisation age of the protolith that are the same within error, 1.74 Ga. This is more than 200 m. y. earlier than the Danopolonian orogeny (1.50-1.45 Ga). The zircon U-Pb ages provide a basis for a new interpretation of the Slupsk gneiss and thus the Late Paleoproterozoic regional correlations across the Baltic sea. The gneiss probably correlates with metaigneous rocks of the Blekinge Province [1] of southern Sweden, which record crust forming events at 1.77-1.75 Ga related to subduction along the southern edge of Fennoscandia. In contrast to the likewise coeval granitoids of the Transcandinavian Igneous Belt, the foliated 'gneissic' granitoids of Blekinge Province and the basement rock at Slupsk borehole are deformed. This proposed correlation between crystalline basement rocks from opposite sides of Baltic Sea is supported by similarities in the T (Nd)<sub>D</sub> model ages of juvenile crust in the two areas, 1.99-1.98 Ga.

[1] Johansson et al. (2006) GFF 128, 287-302.

## Density functional theory simulation of acid hydrolysis of an SiOSi linkage on the (101) surface of α-quartz

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The phenomenon of silicate dissolution has been studied and modeled with quantum mechanical calculations for decades. However, due to computational limitations early calculations did not include solvation effects at the mineralwater interface nor the structure of the mineral. Advances in hardware and software have now made it possible to include the mineral structure and explicitly model the mineral-water interface on the scale of a few nanometers.

This work focuses on the common mineral and model system  $SiO_2-H_2O$ -HCl. Hydrolysis of Si-O-Si linkages are thought to control the dissolution of polymerized silicates, so focusing on this reaction has implications for weathering of a wide variety of rock types. The inclusion of a solution phase in these simulations will allow the results to be contrasted against previous studies where solvation was absent or limited. HCl was added to the system to simulate the effect of low pH on the dissolution which has been experimentally observed to increase rates dramatically. The fact that a Cl<sup>-</sup> ion is used to charge balance the model system is used to explore the effects that counterions in the electrical double layer have on the structure and energetics of the H<sup>+</sup>-catalyzed hydrolysis reaction.

Structures of the  $\alpha$ -quartz (101)-water model system calculated with periodic DFT molecular dynamics are consistent with experimental observation as a first test of the modeling methodology. The SiO<sub>2</sub>-H<sub>2</sub>O model was then constrained to protonate an Si-O-Si linkage which lengthened the Si-O bonds at this site but raised the system energy unrealistically. Addition of HCl to the system lowered the energy to form the protonated Si-O-Si linkage significantly. A pathway to protonation of this linkage and subsequent hydrolysis based on formation of a H-bond from a nearby Si-OH group is predicted to have a relatively low-energy barrier of activation. The Cl<sup>-</sup> was found to play a role in stabilizing the protonated Si-O-Si linkage by providing local charge balance within the electrical double layer. Using these DFT simulations to train and test a reactive force field for larger simulations will also be discussed.

## Lunar space weathering via exposure to ultraviolet radiation

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We are currently investigating space weathering due to ultraviolet (UV) irradiation on the Moon. The Moon receives approximately 116 W/m<sup>2</sup> [1], but, to our knowledge, it has been considered negligible in its contribution to lunar space weathering. Our spectra (Figure 1) obtained before and after irradiating San Carlos olivine with UV in a vacuum demonstrate many of the same spectral features associated with space weathering by the solar wind and/or micrometeorite impacts. Olivine samples were exposed to UV irradiation from a Newport Solar Simulator with a power density of about 1223  $\bar{W}/m^2$  through a quartz window for varying times up to 594 hours while under a vacuum of approx. 10<sup>-6</sup> torr. The reflectance spectra obtained at RELAB demonstrate the distinct reddening and darkening of spaceweathered olivine surfaces as well as the suppression of the spin-forbidden absorption bands at about 450 nm in the silicate structure. This form of space weathering appears to occur for even modest ultraviolet wavelengths with enough energy to break chemical bonds (e.g. a 100 nm photon carries 12.4 eV of energy while the Si-O bond in quartz is only 6.4 eV).



**Figure 1.** Before and after visible-NIR spectra of two San Carlos olivines. The spectra are offset by a relative intensity of 0.10 for clarity.

[1] Arvesen, J.C. et al. (1969) Applied Optics 8 2215–2232.

## Consistent treatment of 'denticity' in surface complexation models

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Spectroscopic studies and atomistic simulations of (hydr)oxide surfaces, which show that some aqueous cations bind to two or four surface oxygen atoms, have increased interest in multi-dentate surface complexation models (SCMs) [1-3]. However, it remains unclear how the (fitted) values of intrinsic equilibrium constants  $K_M^{\text{int}}$  (referenced to infinite dilution) for  $\delta$ -dentate M surface-binding reactions ( $\delta > 1$ ) depend on the choice of concentration scale. In existing SCM codes, a surface complex may be treated in scales of either: molarity/molality ([]); site coverage fraction ( $\theta$ ); surface mole fraction (x); molecular surface density ( $\Gamma$ , in mol·m<sup>-2</sup>); or relative density  $\Gamma/\Gamma_{o}$  (o, where  $\Gamma_{o} = 2 \cdot 10^{-5} \text{ mol} \cdot \text{m}^{-2}$  is the reference adsorbed density [4]). Our aim was to investigate, for 'denticities'  $1 \le \delta \le 4$ , how to convert the  $K^{int,\delta}$  values fitted for a given titration data set (the same solid concentration  $c_{s}$ , specific surface area  $A_s$ , and monolayer site density  $\Gamma_c$ ) between different concentration scales.

For single-site monodentate surface binding reactions,  $K_M^{\text{int}}$  expressed in all concentration scales ([],  $\theta$ , x,  $\Gamma$ , o) reduce to the same value  $K_M^{\text{int,1}}$ . For the binding with  $\delta \ge 2$ , conversion factors from  ${}^{x}K_M^{\text{int,0}}$  to  ${}^{\theta}K_M^{\text{int,0}}$  are about  $\delta$ . From  ${}^{l}K_M^{\text{int,0}}$  to any other scale, they involve  $(c_SA_S\Gamma_C)^{\delta-1}$  which is ca.  $10^{-5}$  for  $\delta = 2$  or  $10^{-15}$  for  $\delta = 4$  at typical  $c_s = 1$  g·dm<sup>-3</sup>,  $A_s = 10$  m<sup>2</sup>g<sup>-1</sup>, and  $\Gamma_C = 10^{-6}$  mol·m<sup>-2</sup>. Conversions of  $K^{int}$  from [],  $\theta$  and x scales into the  $\Gamma$  scale involve  $(\Gamma_C)^{1-\delta}$ , which has a value ranging from  $10^5$  to  $10^{18}$  at  $10^{-6} < \Gamma_C < 10^{-5}$  mol·m<sup>-2</sup>. The  $K^{int}$  conversions from [],  $\theta$  and x to the o scale include  $(\Gamma_o/\Gamma_C)^{\delta-1}$  which vanishes if  $\Gamma_C = \Gamma_o$  (then  ${}^{o}K_M^{\text{int,0}} = {}^{s}K_M^{\text{int,0}}$ ).

Our findings show that the use of published  $K_M^{int,\delta}$  ( $\delta \ge 2$ ) in SCMs may lead to erroneous results, if concentration scales are not precisely defined both in the original fitting and in the subsequent application. At trace ion concentrations, using formally monodentate surface species would be safe especially on 'strong' sites, for which the density is typically adjusted to reproduce multi-site isotherms. Our results from comparative fitting of  $K_M^{int,\delta}$  with SCM codes using different scales show the magnitudes of 'denticity effects'; we discuss ways to correct for these effects in re-using, comparing or correlating values of  $K_M^{int,\delta}$ . In a further thermodynamic treatment, e.g. deriving the entropy effect of the adsorption reaction from  $K_M^{int,\delta}$  fitted for different temperatures, the constants must first be made dimensionless and independent of  $\delta$  and  $\Gamma_C$  by converting them into the (o) scale.

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 Kulik (2006) Interf. Sci. Technol. 11, 171–250.

## Geochemistry of lavas from Barren Island volcano, Andaman Sea

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Barren Island (BI) (12.29°N, 93.85°E) of Andaman and Nicobar Islands, India is the only subaerial active volcano of the Andaman Subduction Zone, and is one of the northernmost volcanoes of the Indonesian Arc. Located on the Burmese plate, which overrides the Indian plate, this stratovolcano is believed to have emanated from the ocean floor during the Pleistocene [1-2]. It has had historic subaerial eruptions during 1787-1832 and has been active since 1991 [1-2].

Study of the Nd-Sr isotopic, trace element and major element characteristics of lava, scoria and ash from the volcano provides insights into the nature of the magma chamber, and the mantle source. Major element analyses of these samples reveal that most volcanics are less to moderately evolved basalts or basaltic andesites (Mg# = 43.5-68.1) of subalkalic nature (SiO<sub>2</sub> = 47-57 wt%, Na<sub>2</sub>O+K<sub>2</sub>O < 5.1 wt %,). The high alumina content of a majority of samples (Al<sub>2</sub>O<sub>3</sub> > 20 wt %) possibly hints at dissolution of xenocrystic plagioclase, derived from plutonic rocks present in the magma chamber [1]. Alternatively, this could indicate a shallow mantle source for these volcanics.

Primitive mantle normalized trace element patterns of BI samples indicate that these lavas represent typical subduction zone magmas. They show large relative Nb, Ta and Ti depletions and strong relative enrichments in K and Pb, with lesser enrichment of Sr. 87Sr/86Sr of BI lavas vary from 0.70379 to 0.70415, and  $^{143}\text{Nd}/^{144}\text{Nd}$  range from 0.512861 ( $\epsilon_{\text{Nd}}$ = 4.4) to 0.512992 ( $\epsilon_{Nd}$  = 6.9). These data suggest that the BI lavas are derived from a large ion lithophile element (LILE) depleted source, and that the mantle source is marginally enriched in LILE compared to the Indian-Mid Oceanic Ridge Basalts (I-MORB). Our results suggest that BI magmas are the most primitive in comparison to that of all other volcanoes of the Indonesian Arc [3]. Mixing calculations suggest that the material contribution from the Indian plate slab to the BI magmas is < 10%. This conclusion is also supported by low Th/Ce ratios (< 0.12) of the lavas.

[1] Luhr & Haldar (2006) J. Volcano. Geotherm. Res. 149, 177–212. [2] Sheth et al. (2009) Bull. Volcano. 71, 1021–1031. [3] Turner & Foden (2001) Contrib. Miner. Petrol. 142, 43–57.

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We present here for the first time the temperature dependence of electron paramagnetic resonance studies on the naturally occurring calumetite from a copper mine, Rajasthan, India, in the low-temperature range of 120 to 295 K, using JEOL-FE-IX ESR spectrometer [1]. The composition of the prepared sample is determined as CuO (52.84 wt % to 52.46 wt %); Cl (23.16 to 23.54 wt %) and the loss of ignition is about 24 wt %. The room temperature EPR spectrum of calumetite exhibits one intense, unresolved parallel component centered at  $g_{II} = 2.235$  and three well resolved perpendicular components centered at g = 2.111. These resonance signals are a characteristic of Cu<sup>2+</sup> ions in distorted octahedral symmetry. The EPR spectra have also been recorded at low temperatures in 123-295 K range. The intensity of the resonance signals is found to increase gradually with decrease in temperature in 123-295 K range. The population of spin is found to increase with decrease in temperature obeying the Boltzmann distribution law. DTA trace shows two endothermic reactions at about 378 and 598 K, which are attributed to dehydration of the sample. The exothermic peak at about 650 K is due to solid -soli phase transition, which is typically observed in any hydrous minerals [2]. Therogravimetric analyses (TG) data demonstrates the weight loss of the sample up to 24 wt % in the temperature region of 600 to 700 K, the value agrees with the compositional data. Temperature induced dehydration occur in different stages viz., first at about 380 K, with a loss of 5 % weight loss and the second reaction at about 600 K with a weight loss of 10 %. The present study reports for the first time the thermal phase stability of the sample up to 700 K.

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## Effect of land use changes on rainfallrunoff and runoff-sediment relationships in Gaula catchment of Himalayan region

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Land use change is expected to have a greater impact on gully erosion than climate change. Land uses exert a significant influence on the relations of rainfall-runoff and/or runoff-sediment and alter soil and water loss accordingly. Study of the land use changes and their effects on runoff and sediment patterns for the watershed level are essential in water resource planning and management. This study provides an approach to identify the effects of land-use changes on rainfall-runoff and runoff-sediment relations in Gaula catchment of Himalayan region. The study was based on the comparison of the effect of land-use changes during the periods, 1962-63, 1973, 1985-86, and 2005-06. The study objectives were to identify the change of land-use in that years and analyze its effects on rainfall-runoff and runoff-sediment relationships. In this study, double mass curve with trend curve have been used to examine the effect of land use changes on rainfall-runoff and runoff-sediment relationships. The results showed that the land-use change can be considered as main reason for increased runoff and sediment in the catchment. The annual rainfall, annual runoff and sediment load for the period 1958-2005 are investigated. The annual slope of trend curve (STC) of rainfall-runoff in 1968-1977 is more than that in 1958-1967, 1978-1986 and 1986-2005. It represents the accumulative annual runoff increases more rapidly from 1968 to 1977 than that from 1958-1967, 1978-1986 and 1998-2005. The runoff yield in 1968-1977 is more than that in the other comparative series with similar rainfall. The runoff-sediment relationship exhibits that more runoff and sedimentation occurred in the period 1996-2005 than the other periods. The change of land-use in the study periods altered the rainfall-runoff and runoff-sediment relationships.

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Groundwater bioremediation has emerged as a potential research interest in recent years. Moreover, different metallic particles has been tested as possible tool in groundwater treatment. ZVI (Zero Valent Iron) has already been proved highly efficient in treating contaminant like arsenic and chlorinated compounds but not much explored with metal removal, for which SRB (Sulfate Reducing Bacteria) is widely studied and trusted option. Redox potential and pH always play an important role in success of any in situ bioremediation process. In most cases extra substrate and considerable time is needed to start biological reduction. ZVI can play an important role in stimulating anaerobic degradation faster by depleting O<sub>2</sub> and producing H<sub>2</sub> during anaerobic corrosion, which marks an increase in pH and decrease in redox potential. Both of these technologies (ZVI and SRB) can possibly lead to new developments in groundwater remediation if used synergistically, the option which is very less explored yet.

In this study we used different ZVIs to stimulate SRB in low pH groundwater. Molecular tools were used to identify microbial communities, precipitates were characterized using different techniques like SEM and XRD. Stability of precipitates was compared in different pH and redox conditions. Our results indicate that bioaugumentation of ZVI can be very effective in wide range of contaminant removal and forming more stable precipitates, which is always a key parameter while dealing with groundwater remediation processes.

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## Comparison of vibrations of water on rutile and cassiterite surface

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The vibrational spectrum of water is modified by the interface with oxides. This variation in the vibrational properties of the liquid serves as a probe of the interactions at play. We use large scale ab-initio molecular dynamics (AIMD) simulations to study the vibrational density of states (VDOS) of water on rutile (110) surface (titanium dioxide) and cassiterite (110) surface (tin dioxide). The velocityvelocity auto correlation function, calculated from the long trajectories of AIMD simulations, is used to extract the VDOS of water for these systems. The calculated total VDOS of water from our simulation (Figure 1) is in good agreement [1] with Inelastic Neutron Scattering (INS) experiment [2, 3]. The stretching band of the total VDOS of water shifts to a lower frequency for cassiterite surface in comparison to rutile surface. We will show that the microscopic analysis of our simulation reveals that this red shift in stretching band frequency is due to the stronger hydrogen bond formation on the cassiterite surface. This also causes the water on cassiterite to be closer to the surface than on rutile.



**Figure 1:** Computed total VDOS of water on cassiterite (in gray) and rutile (in black) surface.

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## Self-accumulation of aromatics at oil-water interface: A molecular dynamics study

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The interface between two immiscible liquids is a noncentrosymmetric environment about which we know very little in comparison with other condensed-matter materials and their surfaces. Experimental probes of liquid-liquid interfaces are limited because of the relatively small size---typically only a few molecular diameters wide and the buried nature of the interface. Here we have investigated the water and a light-oil model interface. It was found that aromatics concentrate on the interfacial regions, whereas the other hydrocarbons of oil are uniformly distributed along the oil slab. We attributed the self-accumulation of the aromatics to the favorable Gibbs free energy due to the lower interfacial tension between the aromatics-water interfaces. Further, we suggest that the 'weak hydrogen bonding' between the aromatic rings and the proton of the water are the cause of the lower interfacial tension among others.

## First principles simulations of liquidvapor interfaces: Structures, dynamics and chemical reactivity

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Aqueous interfaces are ubiquitous and fundamentally important in understanding many atmospheric, biological, and geological systems. In realistic environments, presence of impurities or surfactants can subtlely change many interfacial properties. Naturally, many experimental and theoretically studies has utilized small amphiphilic molecules like methanol to serve as a model surfactant while probing the liquid-vapor interface in order to understand how surfactants can alter different interfacial properties. Here, we will utilize first principles simulations using density functional theory with various exchange and correlation functionals as well as van der Waals corrections. The accuracy of first principles simulations utilizing different sampling techniques (MD and MC) in predicting bulk properties of a range of fluids will first be discussed. Second, structural and dynamical changes at the interface as a function of increase methanol coverage will be presented. Last, how interfacial water can affect and alter reaction kinetics in the vicinity of the interface will be shown.

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## Trace and rare-earth element altered and mineralized rocks in the Attepe Iron deposits (Feke-Adana, Southern Turkey)

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Hydrothermal-metasomatic iron ores consisting mainly of siderite, ankerite and hematite are located in the Lower to Middle Cambrian limestone marbles of the Eastern Taurus Belt. The siderite, ankerite and hematite ore and host rock samples from the deposits have been investigated for major and trace elements to evaluate the element mobility and mass transfer during fluid-rock interactions.

The (Fe+Mn) concentrations regularly increase, and the (Ca+Mg+TC) contents progressively decrease from the host rock through ankerite, siderite, and hematite ores with increasing chemical index of metasomatism (CIM) values. The host limestone exhibits a positive Eu anomaly (2 to 3.45) and negative Ce anomalies (0.59 to 0.96). This limestone has much lower REE contents (3.92 ppm) than the PAAS (184.77 ppm). The elements of Cr, Y, Tb, Ho, and Lu behaved as immobile. The altered (ankerite) and mineralized rocks (siderite and hematite) were enriched in Fe, Mn, Ba and depleted in Ca, Mg, Si, Al, K, Na, Ti, and P. The average REE contents of the ore samples (9.13 to 12.01 ppm, mean=10.44 ppm) are higher than those of the host rock, but significantly lower than in the PAAS. Most of the REE were mobilized and fractionated. The LREE were strongly depleted, and HREE were slightly enriched. MREE show different behaviors in different sample groups.

The (La/Lu)N ratios show a decreasing trend from the host rock to siderite, ankerite, and hematite ores with increasing HREE and decreasing LREE contents. The ore samples show positive Eu (1.61 to 8.86) anomalies and negative Ce anomalies (0.34 and 0.98). Three samples display positive Ce (1.06-1.09) anomalies. In the ore samples, HFSE such as Ti, Zr, and P were depleted, as were LILE, e.g. K, Th, U, Pb, La, and Ce and TRTE, e.g. Cu, Ni, and Zn, elements. The Ba and Sr demonstrate dissimilar behavior. Ba was enriched, while Sr was depleted.

## Crystallographic control of sheet silicate dissolution

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We present an experimental and theoretical study of sheet silicate dissolution kinetics. Sheet silicates have a layered structure that significantly affects the dissolution mechanism and rates. Dissolution of mineral powders [1, 2] revealed a high variability in rates of 2-3 orders of magnitude, typically thought to reflect variation in basal to lateral surface area ratio. Although AFM studies also document the differential reactivity of basal and lateral faces [3, 4], the contributions of basal and lateral surfaces to total rate are not yet well understood. Our study focuses exclusively on the role that layered structure plays in the dissolution mechanism and the related variation in rates. We use vertical scanning interferometry to observe the dissolving mineral surface and measure dissolution rates. This approach allows us to obtain precise rates at specific faces (basal or lateral) over a large surface area. Our experimental results in concert with kinetic Monte Carlo simulations help to develop and test a theoretical model of sheet silicate dissolution kinetics.



Figure 1: Dissolving mica edge face (VSI data).

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## Marine osmium isotopic records in the Triassic-Jurassic deep-sea sediments of Panthalassa

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Attention has been focused on relationships between massive volcanic eruptions and major environmental perturbations [1]. The Triassic-Jurassic (T-J) transition at c. a. 200 Ma marks one of the five biggest extinctions in the Phanerozoic when a substantial proportion of marine and terrestrial species became extinct. It also marks extensive magmatic activities associated with the emplacement of Central Atlantic Magmatic Province (CAMP). Massive eruption has been implicated as a possible forcing mechanism for the climatic and biotic changes at the T-J boundary. However, the mechanism triggering the T-J mass extinction is still controversial.

Since seawater Os isotopic composition varies in response to change in relative rates of Os supply from continental crust, mantle and cosmic dusts [2], Os isotopic record from hydrogenous fraction of marine sediment has been thought to be a valid tool for reconstructing temporal changes in relative supply rates of Os from these sources. Although Os isotopic ratios across the T-J boundary have been reported from British sites [3], no data has been reported from Pacific (Panthalassa) pelagic basin. We present a high-resolution Os isotopic record across the T-J boundary, extructed from a bedded chert succession deposited on a Panthalassa deep basin (Inuvama Chert [4]). Our new dataset shows a gradual decrease through the Rhaetian, and subsequent stepwise increases across the T-J boundary. The gradual decrease in Os isotopic composition through Rhaetian suggests an increase in relative supply rate of unradiogenic Os from the CAMP, and the subsequent stepwise positive shifts may have been caused by a rapid increase in relative supply rate of radiogenic Os due to an enhanced continental weathering. In the presentation we will discuss paleoenvironmental implications of the Os isotopic changes.

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## Diversity hidden in the dark – Microbial communities involved in carbonate mineralization in the Blessberg Cave, Germany

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Caves provide a unique habitat for investigating belowground biodiversity and the potential role of microbes in carbonate mineral formation. The Blessberg Cave (developed along the south fault of the Thuringian Forest in triassic limestone) in eastern Germany was discovered in 2008 and transiently available for scientific investigation in 2008 and 2009. This hidden habitat was the focus of microbial diversity investigations and characterization of minerals and bacterial biomineralization.

Mineral composition of stalagtite and cave sediment material was investigated using X-ray diffraction (XRD), verifying the presence of quartz, kaolinite and micaceous minerals. Visualization by confocal laser scanning microscopy (CLSM) revealed low cell numbers within and on the stalagtite surface. Clone sequences are being analyzed to explore the diversity of stalagtite bacterial communities. Bacteria isolated on oligotrophic and carbonate precipitating medium from sediment samples were members of ubigitious bacterial groups, e.g. β- and γ-Proteobacteria, Actinobacteria and Bacteroidetes. The carbonate-precipitating capability of isolates was tested in liquid carbonate-precipitating medium. Two isolates, identified as Arthrobacter and Rhodococcus sp. produced precipitates and were visualized by scanning electron microscopy (SEM) and CLSM. Mineral composition, analyzed by XRD and energy dispersive X-ray analysis (EDX), showed a poorly crystalline material, not identified as calcite. Analysis of 16S rDNA of the in situ bacterial communities revealed a great, yet unexplored diversity in the Blessberg Cave. The  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -Proteobacteria subgroups, as well as the phyla Bacteroidetes, Acidobacteria, Nitrospirae, Chloroflexi, Planctomycetes, Verrucomicrobia, Actinobacteria and Firmicutes were detected. A high number of the clones was affiliated with uncultured bacterial clones described from diverse environmental samples, e.g. karstic groundwater, cave wall biofilms, oligotrophic sea sediment. This study gave insight into the structure of the indigenous cave bacterial communites, harboring potential for biomineralization.

## Effects of magma hybridization and late-magmatic fluids on zircon in a Variscan post-collisional pluton

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The ca. 315-304Ma [1] Karkonosze pluton of the Bohemian Massif comprises a sequence of intrusive facies that progress from porphyritic and equigranular granites with mafic microgranular enclaves (MMEs), through to hybrid granodiorite, with multistage emplacement of composite dikes. Progressive hybridization of fractionating, crustal-derived, felsic magma with injections of upper mantle/lower crustal-derived mafic (lamprophyric) magma has been recognized from elemental and isotopic geochemistry [2]. Such complexity is reflected in a variation in published isotopic ages (328-300Ma) from both bulk geochemical and accessory mineral analysis; however, there are no clear relationships to the sequence of intrusions observed.

To resolve this issue, zircon in various facies were analyzed by SIMS and electron microprobe, supported by submicron element mapping by field emission electron microprobe [1]. With increasing degrees of hybridization, zircon morphologies diverge from simple, oscillatory-zoned forms typical of growth in a fractionating magma, to grains modified by solid-state dissolution and reprecipitation, and clustered, convolute and skeletal forms characteristic of both quench crystallization and fluid-assisted reequilibration (especially in composite dykes and MMEs. High Th-U contents, metamictization, alteration and recrystallization all play a role in producing variable ages. When accounted for, a sequence of magmatic and fluid events can be revealed: ca. 315Ma for zircon crystallization in fractionating granitic magmas and quench growth in mafic microgranular enclaves; 312-309Ma quench growth and modification by fluid-rich melt in hybrid magmas and composite dikes; and 304 Ma for reequilibration of altered and repreciptitated zircon in MMEs by late-stage magmatically-derived fluids [1].

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## Geochemical modeling of slab-derived fluids

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The main aim of this study is to contribute to better understanding of fluid processes occurring in subduction zones with a comprehensive framework involving slabderived fluids to near-surface fluids such as seawater, meteoric water and hot spring waters. Several studies estimated the contribution of slab-derived fluids to island-arc magmatism (e.g. [1]). In non-volcanic or forearc regions, their involvements have been hardly found. One exception, however, could be the so-called 'Arima-type brine', highly carbonated, non-volcanogenic hot springs with extreme high salinity, welling up in the Kinki district, SW Japan.

Our previous analytical research on these hot springs identified and characterized the concentrated 'source' brine in a robust multi-elemental/isotopic space, and so far, supports the idea that NaCl-CO<sub>2</sub>-rich aqueous fluids, which are possibly slab-derived fluids originated from subducting oceanic crusts, might have uprisen from a deep part of the forearc region and might supply solutes, gases and water itself to the brine.

Combined with numerically estimated chemical and isotopic characteristics of slab-derived fluids, the <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.70873 of the observed source brine is close to the predicted value of the Philippine Sea slab-derived fluid, i.e. 0.709492 [1], and distinct from that of the Pacific slab-derived fluid, i.e. 0.704762 [1]. Furthermore, our numerical model to calculate hydrogen and oxygen isotopic ratios of dehydrated fluids also suggests that their isotopic ratios become close to observationally estimated values of the Arima-type brine at about 50 km depth, which coincides with the depth of the Philippine Sea plate beneath the studied area.

Here we present our recent results from further numerical modeling of geochemistry of slab-derived fluids with interpretations of Pb and Li isotope analyses of the brine, and will discuss their possible contributions to near-surface fluids in subduction zone systems.

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## Abyssal abiogenic origin of petroleum: Updated milestones

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A number of facts obtained during the last decades such as location of ultra-deep petroleum fields below 'the main zone of petroleum formation', impossibility to identify biotic sources of the hydrocarbon generation for most of supergiant oil and gas accumulations, biomarkers recognized in meteorites, presence of hydrocarbons on the planets of the solar system and in space cannot be convincingly explained from the biotic concept of petroleum origin point of view. At the same time all these facts have found a proper interpretation in the frame the theory of the abyssal abiogenic origin of petroleum. According to this theory hydrocarbon compounds are generated in the mantle and migrate through the deep faults into the Earth's crust where they form oil and gas deposits in any kind of rock. The accumulation of oil and gas is considered as a part of the natural process of the Earth's outgrassing, which was in turn responsible for creation of its hydrosphere, atmosphere and biosphere. Experimental results obtained recently [1, 2] place the theory of the abyssal abiogenic origin of petroleum in the mainstream of modern physics and chemistry and open a great practical application.

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## Allophane and palagonite as the product of volcanic glass alteration of different ages

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Volcanic cinders and ashes of different ages and compositions have been collected in the Kluchevskaya volcano group on Kamchatka and in Iceland. Experimental study of thermal properties and phase composition of water was performed [1, 2]. There is no unfrozen water in the investigated modern volcanic cinders from Kamchatka in all temperature ranges (from -15 to 0°C). But for volcanic ashes unfrozen water content is fixed from 0, 4 to 11% at -5°C that depends on age.

Four samples of ashes have been chosen for researches: three of them (no. 1-3) are collected on Kluchevskaya volcano group (Kamchatka), and one (no. 4) – in the south of Iceland. Ash samples had different age: no. 1 – about 35 years, no. 2 – about 1500 years, no. 3 – about 2000 years, no. - 15000-150000 years.

IR-spectroscopy study (IR-fourier spectrometer FSM-1201, Russia) was made for diagnostics of mineral compositions of ashes. As the results there were found that the sample no. 1 was the waterless allophone, the samples no. 2, 3 – were allophanes with the various water contents and the sample no. 4 – palagonite (Peng Wenshi, 1982; Geptner, 1977).

The thermal study showed that the mass loss depends directly on the ages of the investigated samples. The content of absorbed and structure water were found as: sample no. 1 -  $0\% \pm 0\%$ , sample no. 2 - 1,  $0\% \pm 2$ , 8%, sample no. 3 - 3, 5%  $\pm 2$ , 7%, sample no. 4 - 6, 3%  $\mu$  5, 3%.

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## Monitoring dissolved gases and ions in groundwater using an *in situ* sampling technique

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We tested an in situ method for monitoring the concentrations of aqueous chemical species and dissolved gases in groundwater. We deployed in situ samplers in 8 wells completed in the glacial Glasford formation and underlying Banner formation of the Mahomet aquifer, a regional water supply in east-central Illinois. We distributed and retrieved samplers 25 times over 35 weeks. At one point in this interval, we pumped each well to retrieve a sample for standard analysis, for comparison to results obtained by the in situ technique. The in situ method relies on the diffusion of analytes through a permeable membrane integral to our samplers. The samplers can be deployed and retrieved from a well without the necessity of pumping groundwater. Since no pumping is required, the method allowed the samplers to be monitored from all of the wells within a few hours.  $SO_4^{2}$ concentrations ranged among the wells from below detection (0.01 mM) to 0.84 mM, and Cl<sup>-</sup> ranged from 0.01 to 3.08 mM. These results correspond closely to concentrations measured from pumped samples. Over the first 21 weeks, H<sub>2</sub>, CO<sub>2</sub>, and  $CH_4$  averaged 42.5 nM, 0.012 atm, and 0.090 atm, respectively. At 21 weeks, about the time we pumped the wells, we observed that H<sub>2</sub> increased by a factor of 5, and CH<sub>4</sub> by a factor of 3, in two wells screened in the Glasford formation and three wells screened in the Banner formation. Measurements conducted in the remaining three wells changed little. The concentration of CO<sub>2</sub> in each well remained constant throughout the sampling period in each well. The in situ method may provide a useful technique for frequently testing groundwater chemistry over extended periods of time.

## Investigation of matrix fluids in fractured aquifers through various gas analyses

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We investigated the matrix fluids in a fractured aquifer in French Brittany (Ploemeur, national observatory site). We used four wells close to each others, two of them being pumped for several hours. The four wells were monitored during the whole experiment for chemical composition (major and trace elements) and dissolved gases content: CFC, SF<sub>6</sub>, Rn, noble gases and He isotopes. After an equilibration phase, the chemical and gas concentrations evolve during the relaxation phase following pumping. The production of matrix fluids is evidenced through the following observations:

• CFC concentrations decrease, indicating waters with longer residence time;

• He, Rn and  $SF_6$  concentrations increase with time, indicating a potential production mechanism.  $SF_6$  and Rn production have indeed been measured in this aquifer. However, it is interesting to notice that these three elements do not have the same reactivity. they do not have similar production mechanisms and diffusion coefficients;

• Some chemical elements such as silica increase indicating silicate alteration processes;

• The redox conditions also vary with time during the relaxation phase, indicating more reduced conditions with U concentration increases;

 $\bullet$  Ar increases also indicate either an Ar production or a recharge temperature of 5°C.

This experiment shows that fluids with various compositions in fractured aquifers are related to various degree of micro- and macro-porosity, and may be associated to various pumping conditions.