

¹²⁹I as atmospheric tracer

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Iodine is an important element in oceanic, atmospheric and terrestrial systems. Atmosphere is one of the most important compartments for natural and anthropogenic changes and provides rapid response to disequilibrium. Iodine is transferred between compartments on different time scales and in different chemical forms (species). However, the dominant transfer pathway is either through the atmosphere as reactive gases (e.g. I₂, CH₂I₂, CH₂Cl, CH₃I), bound to aerosols or in the aqueous phase (i.e. rain, rivers, lakes and oceans).

¹²⁹I has received increased attention in recent years as unique atmospheric and environmental tracer. ¹²⁹I is a long lived (T_{1/2} = 15.7 Ma) radionuclide whose concentration in environment has been elevated by several orders of magnitude, mainly by emission from reprocessing plants [1]. However in spite of environmental relevance, there is still little knowledge about temporal variability of the ¹²⁹I anthropogenic fallout over Europe. One of the main goals of this study is to trace transport path of ¹²⁹I released from reprocessing plants in atmosphere by measuring its concentration.

This study deals with temporal changes of iodine isotopes (¹²⁷I and ¹²⁹I) in aerosols collected within two years in Vienna, Austria (202 m a. s. l). The data shows isotopic ratios of the order of 10⁻⁸ to 10⁻⁷. The predominant basis for the higher ratios in the aerosols appears to be upcurrent sources of ¹²⁹I from nuclear fuel reprocessing plant at Sellafield. Apart from this, short term variability of ¹²⁹I concentrations was associated with air mass transfer and wind pattern.

[1] Tania Jabbar, Peter Steier, Gabriele Wallner, Norbert Kandler & Christian Katzlberger (2011) 'AMS analysis of iodine-129 in aerosols from Austria' *NIMSB* (accepted).

Mineral composition of particulate matter in human lung samples from Upper Silesia (Poland) – Preliminary results

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The aim of this study is to compare the mineral composition of airborne particles to mineral composition of particles inhaled by humans who lived in highly urbanized and industrialized region of Upper Silesia (S Poland). The characterization of mineral particles in samples of lung tissues of 40 subjects by TEM and ASEM revealed the presence of quartz, aluminosilicates including feldspars, Ca carbonates, iron oxides, Ca sulphates, and kaolinite as major components.

All of those minerals are major mineral constituents of dust particles in Upper Silesia in addition to soot. Some of them may serve as tracers of the source of inhaled particles. For instance, barite particles in lung tissues may be related to the abundant airborne barite resulted from the combustion of the uniquely Ba-rich Silesian coal. The lung tissues lack of Pb-particles, which are common in airborne soot particles. Their fast dissolution in lung fluids is a possible explanation of their absence in lung tissues.

Additionally, Ca-phosphates (perhaps of the apatite group) and zinc oxide were observed on rare occasions in lung tissues.

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Direct ventilation of the North Pacific did not reach 2300 m during the last glacial termination

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It has recently been argued that the North Pacific circulation during HS1 (18-14.6 kyr) was distinct from both the LGM and the warmer intervals that followed, with a greater formation of 'deep waters' sinking to 2500-3000 m. This intriguing conjecture appears to be inconsistent with a number of geochemical proxies measured at multiple North Pacific core sites from this depth range.

'Ventilation' involves the input of atmospherically-equilibrated waters to the ocean interior. Well-equilibrated waters have high concentrations of oxygen and relatively low concentrations of dissolved carbon dioxide. Bottom waters with high oxygen concentrations inhibit the diagenetic enrichments of some redox-sensitive trace metals in underlying sediments, while low concentrations of carbon dioxide (relative to alkalinity) produce high carbonate ion concentrations, encouraging preservation of calcium carbonate (CaCO₃) microfossils in sediment. Thus, poorly ventilated bottom waters are likely to show both sedimentary authigenic U enrichments and poor CaCO₃ preservation. Measurements at sites from the NW Pacific and in the Bering Sea show that, at 2393 m and 2209 m water depth, respectively, these twin hallmarks of poor ventilation reigned throughout the LGM and HS1, to finally disappear after ~15 ka. This sequence of change is consistent with a poorly ventilated deep ocean throughout this interval that extended from the abyss to within < 2500 m of the surface. The assembled evidence does not appear to provide an opening during the deglaciation during which the North Pacific water could have pumped oxygenated waters into the deep.

A new starting point for the mantle's geochemical reservoirs

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The present-day terrestrial mantle, as sampled by melts that erupt at the surface, is chemically and isotopically heterogeneous. The discovery of a surviving portion of the early-formed silicate Earth that existed immediately after formation of the core—referred to as primitive mantle—would place constraints on the earliest chemical evolution of the Earth. Such a discovery would also provide a starting point to understand the origin and long-term evolution of the various geochemically-distinct mantle reservoirs that now make up Earth's interior. Earth's primitive mantle has long been thought to be compositionally similar to primitive chondrites, at least for the refractory, lithophile elements. However, the recent discovery that modern terrestrial lavas have ¹⁴²Nd/¹⁴⁴Nd ratios ~18 ppm higher than chondrites suggests that the Earth's primitive mantle has a Sm/Nd ratio that is ~5% higher than chondrites [1], and that all modern terrestrial mantle and crustal reservoirs ultimately were derived from this reservoir with superchondritic Sm/Nd. Today, the ¹⁴³Nd/¹⁴⁴Nd of the primitive (albeit non-chondritic) reservoir would be ~0.5130, a ratio that is closer to the depleted MORB mantle than to chondritic. In order to extract the continents from the non-chondritic primitive mantle, the depleted mantle reservoir must comprise > 50% of the mass of the mantle, thus extending into the lower mantle. Another implication of a non-chondritic Earth is that it provides a new reference for the composition of primitive mantle (e.g. ¹⁴³Nd/¹⁴⁴Nd = 0.5130), and reservoirs that were once considered depleted relative to chondritic (e.g. HIMU, with ¹⁴³Nd/¹⁴⁴Nd = 0.51285) are actually enriched relative to the postulated non-chondritic mantle. The observation that the most frequently-occurring ¹⁴³Nd/¹⁴⁴Nd ratio (0.5130, PREMA) in ocean island basalts (OIB), including lavas with high ³He/⁴He, overlaps with the value suggested for a non-chondritic mantle (0.5130) suggest that large portions of the mantle sampled by OIB remain little-modified with respect to ¹⁴³Nd/¹⁴⁴Nd. If the Earth's primitive mantle is not chondritic and a portion has survived in the deep Earth to the present-day, we consider the best candidate to be the mantle reservoir sampled by lavas with the highest ³He/⁴He.

[1] Boyet and Carlson, *Science*, (2005).

A 'hotspot highway' in the S. Pacific

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New deep-sea dredges from the Samoan region provide evidence for three seamounts (Malulu, Papatua [PPT], Waterwitch) and one atoll (Rose) that are not geochemically related to the Samoa hotspot track. We use a plate motion model to show that three non-Samoan hot spots, currently active in the Cook-Austral Islands, are responsible for 10–40 Ma volcanism in the Samoan region. The four 'interloping' volcanoes in the Samoan region exhibit geochemical affinities with the three hot spots. All three hot spots would have left a depleted, viscous, refractory keel that is coupled to the base of the Pacific lithosphere that has been 'rafted' to the Samoan region. Without major modification of the current 'propagating lithospheric cracks' model, it is not clear how such cracks could yield melts from the refractory keel present under the Samoan lithosphere. Instead, a region of buoyantly upwelling mantle, or plume, is suggested to generate the shield stage volcanism in the Samoan region.

Another implication of the Cook-Austral interlopers in the Samoan region is that they may provide the "missing link" to what may be a third long hotspot track in the Pacific, in addition to the Hawaii and Louisville chains. The Hawaii and Louisville hotspots exhibit very different behavior at ~45–50 Ma (the Hawaiian hotspot exhibits a clear "kink", and Louisville exhibits a gradual bend), and it is important to establish a third long-lived hotspot for comparison during this critical time in Pacific tectonics. Plate reconstruction models suggest the Rurutu hotspot track—one of the three hotspots in the Cook-Austral Islands—bends at ~45 Ma and emerges from the Gilbert Islands before trending through Samoa and toward the present-day hot spot location beneath Rurutu. Deep-sea dredging the seamounts in the region predicted to be the ~45 Ma Rurutu "bend" is necessary for evaluating a genetic and temporal link to the Rurutu hotspot.

Quantitative determination and mapping of trace element concentrations in sulfide minerals using LA-ICP-MS

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Quantitative trace-element analysis of sulfide minerals has a number of important applications, including: empirical indication of deposit setting, geo-thermometry and geo-barometry, ore paragenesis studies, indicator mineral surveys, and deportment investigations. However, progress in this field has been hindered by the lack of multi-element sulphide mineral standards for trace-element microbeam techniques and methods for mapping trace element concentration distributions in samples with complex mineralogy.

In this study, element distribution maps have been constructed from time-resolved LA-ICP-MS signal intensity data acquired during multiple, continuous parallel line ablations and lines of edge-to-edge, square spot ablations across selected areas of petrographic sections. The data were deconvoluted, calibrated and digitally combined using in-house software to generate elemental concentrations maps, which provide detailed information on spatial variations of elements within and between sulfide grains and their enclosing minerals.

Determining concentrations in mono-mineralic sampling areas was performed using conventional calibration protocols involving external standardization and normalization using an internal standard, performed on a (mass) scan-by-scan basis. External standardization was achieved using a multi-element synthetic pyrrhotite standard that was prepared by reaction in an evacuated quartz tube of elemental iron and sulfur doped with multi-element aqueous standards. This has been shown to be homogeneous (r. s. d. <10%) for the majority of the 30 doped elements. For complex mineralogies, both sulfide and silicate external standards were employed, together with normalization using different internal standard elements and/or concentrations for different minerals, and algorithms that automatically detected the mineral phase being analyzed.

The effect of different laser sampling strategies and algorithms for data smoothing and interpolation, and assignment of colours to element maps will be demonstrated.

Polycrystalline diamonds witness redox processes in the Earth's mantle

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Polycrystalline diamond aggregates (framesites) from the Orapa kimberlite (Botswana) contain a syngenetic micro- and nano-inclusion suite of magnetite, pyrrhotite, omphacite, garnet, rutile and C-O-H fluid in order of abundance. This suite of inclusions is distinctly different from those in fibrous diamonds, although the presence of sub-micrometer fluid inclusions provides evidence for a similarly important role of fluids in the genesis of polycrystalline diamond. High resolution μ -Computed Tomography (resolution 1.3 μm per voxel) combined with Focused Ion Beam assisted Transmission Electron Microscopy reveals epigenetic replacement coatings of hematite and late stage sheet silicates around magnetites showing that magnetites are often (but not always) interstitial to the diamond and, thus, were open to late stage more oxidized overprinting. We present evidence that the primary paragenesis preceding this late stage event formed from a reduced, water-rich C-O-H fluid oversaturated in carbon upon entering the base of the subcratonic lithosphere along opening cracks. Precipitation of diamond increased the water content of the fluid, fluxing melting of surrounding rocks (eclogitic silicates, Fe-sulfides, oxides), which reprecipitated in the interstices between diamonds and as nano-inclusions. Pyrrhotite crystallization led to a rise in $f\text{O}_2$ in the small-scale Fe-O-S melt, which is amplified by the precipitation of diamond from the C-O-H fluid, moving the whole system towards more oxidizing conditions. Thus, $f\text{O}_2$ conditions were more reducing at the start of diamond precipitation and evolved towards more oxidizing conditions upon cooling and solidification. The inclusion paragenesis was generated in a local small-scale equilibrium system, and is representative only for the redox conditions towards the end of diamond precipitation. It is generally acknowledged that sulfide melts are relatively immobile in the Earth's mantle. Formation of polycrystalline diamond would require only local remobilization and small-scale transport of pre-existing material. Cratonic roots have been episodically impregnated with carbon-rich fluids - small volume melts from mantle sources as well as subducted basaltic material - since Archean times. This process leads to diamond formation at a range of spatial scales.

Diamond-graphite transformation: A NanoSIMS isotope study of diamond-graphite inclusion in zircon from the Kochetav massif

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Diamond from ultrahigh-pressure metamorphic terrains (UHPM) is an important mineralogical indicator of deep lithospheric slab subduction (>150 km) into Earth's mantle. Details about diamond-to-graphite transition occurring during subsequent exhumation are not well understood. Because the structures of diamond and graphite are so dissimilar, it is unlikely that a direct phase transformation would occur in the graphitization process. Heating experiments at $T=1500\text{-}1800^\circ\text{C}$ and ambient pressure showed that diamond is replaced by disordered graphite along planes with a high concentration of dislocations.

In order to better understand the process of diamond-to-graphite transformation we measured C, and N isotopes in an inclusion, comprising graphite with a diamond core, in zircon from the Kochetav massif, Kazakhstan. The inclusion is $\sim 10 \mu\text{m}$ in diameter and consists of a $\sim 3 \mu\text{m}$ diamond core that is surrounded by a graphite rim $\sim 7 \mu\text{m}$ in thickness. The C and N isotopes were measured with a Cameca NanoSIMS-50. Diamond and graphite in the inclusion are isotopically indistinguishable (i.e. $\Delta^{13}\text{C}_{\text{diamond-graphite}}$ and $\Delta^{15}\text{N}_{\text{diamond-graphite}} \approx 0$). The C and N isotopic composition for the entire inclusion is $\delta^{13}\text{C} = -30 \pm 1 \text{‰}$ and $\delta^{15}\text{N} = +0.5 \pm 3 \text{‰}$ respectively, which is in the range of carbon of organic origin.

The distinctive geometry of the diamond-graphite inclusion - the diamond core mantled by graphite - suggests a retrogressive reaction that probably occurred due to decompression during the host rock's exhumation to the Earth's surface from depths > 120-150 km. The lack of intra-mineral isotope fractionation between diamond and graphite for both C and N isotopes suggests that the retrogressive diamond-to-graphite transformation occurred at temperatures above 500°C and pressures less than 4 GPa. Raman spectroscopy studies of this diamond by Smith *et al.* (2011) show the presence of 1624 -1647 cm^{-1} bands which are close to those of disordered graphite. We thus hypothesize that during exhumation diamond was gradually replaced by graphite through an intermediate phase of disordered graphite.

CO₂ evasion from the Greenland Ice Sheet: A new carbon-climate feedback

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Rising greenhouse gas levels may increase global surface temperatures between 1 and 6°C by 2100. Even greater increases are expected for the Arctic, where sea ice reduction, organic matter decomposition in lakes and thawed permafrost, and other positive feedbacks can potentially amplify the global trend. Melting of the Greenland Ice Sheet (GIS) figures prominently in climate change predictions because it will impact albedo, sea level, and possibly, ocean circulation. However, direct carbon cycle feedbacks are poorly constrained. Here, we show that melting of the GIS yields a previously unknown flux of CO₂ that will likely increase in a warmer world. Water emerges from the Russell Glacier in West Greenland with CO₂ partial pressures (pCO₂) 3 – 10X supersaturated with respect to atmospheric equilibrium. This CO₂ likely originates from microbial respiration beneath the GIS. During downstream transport, the chemical weathering of glacial till sequesters 70% of the excess CO₂ as HCO₃⁻ – a carbon sink on human timescales – and the remaining 30% evades to the atmosphere. Scaled to all rivers draining the GIS, the evasion flux of 0.13 Tg C/yr is small by comparison to other atmospheric CO₂ inputs; however, we hypothesize that significant increases could occur as retreat of the ice sheet margin and expansion of moulins exposes meltwater to basal ice with pCO₂ values up to 340X higher than the current atmospheric value. Worst-case model predictions yield evasion fluxes of 100 – 180 Tg C/yr by 2100 depending whether melting increases linearly or exponentially with time. These CO₂ fluxes surpass those reported for Arctic Lakes (20 Tg C/yr) and would increase by 23% those predicted for permafrost thaw (800 – 1100 Tg C/yr). Our findings suggest that Arctic climate change could have a more significant feedback on global climate than currently anticipated.

Along-arc geochemical variations in the Southern Volcanic Zone, Chile

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The origin of enriched isotopic signatures in volcanic rocks from the northern segment of the Southern Volcanic Zone (SVZ) in Chile is controversial. Hildreth and Moorbath [1] argued for crustal assimilation in the context of their MASH model. Stern [2] and recently Kay *et al.* [3], however, proposed that subduction erosion can best explain the increasing enrichment of the magmas from the Miocene to present. We present new trace element and isotope data from young olivine-bearing volcanic rocks along the volcanic front of the SVZ in Chile. We observe systematic spatial variations in Sr, Nd, Hf and Pb isotopic compositions along the arc with the northern part of the Southern Volcanic Zone (NSVZ) having the most enriched signatures. Oxygen isotope data, with one exception, show uniform compositions, close to that expected for the upper mantle. Mixing calculations using O and Sr isotope ratios suggest that the enriched signature of the NSVZ lavas is primarily acquired in the mantle, favoring the subduction erosion model. Crustal assimilation, however, could also affect the composition of these lavas.

[1] Hildreth & Moorbath, (1988) *Contrib. to Mineralogy & Petrology* **98**, 455–489. [2] Stern, C.R. (1991) *Geology* **19**, 78–81. [3] Kay *et al.* (2005) *GSA Bulletin* **117**, 67–88.

Role of three-dimensional mantle flow in magmatism at slab edges

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Adakitic volcanics associated with subduction-transform plate boundaries have been identified in numerous localities, including the eastern Alaska slab edge, the Kamchatka-Aleutian plate boundary corner, the Cascadia-San Andreas transform fault juncture, and the New Hebrides trench-Hunter Ridge [1, 2]. Three-dimensional (3D) models investigating the solid state flow in the mantle due to subduction of a slab edge predict toroidal flow around the slab edge and an upward flow component, which could lead to decompression melting within several hundred kilometers outward of the slab edge as well as contribute to melting of the slab edge. However, the position of the volcanics with respect to the slab edge and associated upwelling in the mantle has only recently been tested in 3D geodynamic models [3, 4]. We use 3D numerical models to investigate the role of rheology and slab geometry on the mantle flow and its implications for anomalous arc volcanism near two slab edges: the eastern Alaska slab edge and the slab edge in the easternmost New Hebrides [3, 5]. In the eastern Alaska region the Aleutian trench terminates at a near right angle into the Fairweather-Queen Charlotte transform boundary. In the eastern New Hebrides, the subduction zone makes a nearly 90 degree arcuate turn, such that the slab edge intersects with the back arc spreading center. The models predict localized rapid mantle velocities (greater than 80 cm/yr), which may contribute to the preservation of primitive magmas that can be brought to the surface. These models do not investigate the link between melt migration and solid state flow of the mantle, which is an important and complex process, but rather aim to place a framework for interpreting how the 3D solid state flow field may influence migration patterns in subduction zones.

[1] Yogodzinski *et al.* (2001) *Nature* **409**, 500–504. [2] Durance (2009) PhD Thesis, Monash University. [3] Jadamec & Billen (2010) *Nature* **465**, 338–341. [4] Schellart (2010) *Geology* **38**, 691–694. [5] McLean (2010) Honors Thesis, Monash University.

The magnitude and composition of the delamination flux in arcs during continental crust formation

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As the bulk continental crust is not in equilibrium with a mantle assemblage significant volumes of mafic/ultramafic composition counterbalancing the andesitic bulk composition of the crust are missing. Significant volumes of such complementary compositions are exposed in the Kohistan Arc, NE Pakistan. We constrain the bulk composition of the Kohistan arc and constrain the volume and composition of rocks needed to balance the andesitic crust composition to a mantle derived melt using the cumulates exposed in Kohistan. The Kohistan bulk arc composition results very similar to global continental crust estimates indicating that modern arc activity is the dominant process that formed the (preserved) continental crust. Fitting the bulk Kohistan arc crust and the ultramafic cumulates exposed at base of the arc (dunites, wehrlites, websterites, cpx-bearing garnetites and hornblendites, and garnet gabbros) to primitive arc melts with calc-alkaline/tholeiitic, alkaline, and boninitic affinity from various island arcs demonstrates that delamination of wehrlites + garnet hornblendites ± garnet gabbros perfectly explains the evolution from a tholeiitic/calc-alkaline primitive high-Mg basalt to the continental crust. Mass balance demonstrates that volumes of delaminate similar or larger to the continental crust are required. Including these ultramafic cumulates into the estimates of mass fluxes at convergent margin significantly increases the volume of magma production rates in convergent margin setting. Compared to depleted mantle, the delaminate is enriched in Pb and low U concentrations (low μ U component) and may compensate for the depleted mantle radiogenic lead composition.

Structure of CaO-Al₂O₃-SiO₂ melts studied by molecular dynamics and diffraction experiments

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The structural characterization of multicomponent liquids is a challenging problem. From the experimental perspective, measurements need to be performed *in situ* at high temperature (and possibly high pressure). Furthermore, a single method such as x-ray or neutron diffraction, Raman or NMR spectroscopy is usually not sufficient to provide a reliable structural model. On the other hand, molecular modeling approaches using classical interatomic potentials often lack accuracy and computationally expensive first-principles simulations suffer from finite size and time effects. It appears attractive to combine the strengths of different techniques to investigate the structure of chemically complex melts and the relation between their structure and their physical or thermodynamic properties.

Calcium aluminosilicate melts and glasses are important in both geological and technological context. Here, we employ advanced classical interaction potentials that were parametrized using electronic structure calculations [1] to predict the structure of representative liquids of the CaO-Al₂O₃-SiO₂ system at ambient pressure and a temperature of 2500 K as a function of chemical composition. The quality of the simulation model is assessed by comparing the computed total static structure factors to data from x-ray and neutron diffraction experiments (e.g. [2]). In this presentation, we will focus on structural changes across the binary CaO-SiO₂ and CaO-Al₂O₃ as well as the metaluminous (CaAl₂O₄)-SiO₂ joins. Similar to the MgO-Al₂O₃ system [3], the average Al coordination decreases from about 4.4 in pure Al₂O₃ melt to 4.0 in Ca-rich melts. At the same time, the number of OAl₃ triclusters is reduced significantly. The distributions of Ca coordination are rather broad but they are dominated by a sixfold octahedral geometry and show a decreasing average coordination towards the Ca-rich melts. In the glass-forming region of the CaO-Al₂O₃ system, a maximum in the melt viscosity is observed well above the glass transition temperature.

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Role of microbe in the formation of illite from nontronite: Mesophilic and thermophilic bacterial reaction

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The formation of illite through the smectite-to-illite (S-I) reaction is considered to be one of the most important mineral reactions occurring during diagenesis. In biologically catalyzed systems, however, this transformation has been suggested to be rapid and to bypass the high temperature and long-time requirements. To understand the factors that promote the S-I reaction, the present study focused on the effects of pH, temperature, solution chemistry, and aging on the S-I reaction in microbially mediated systems. Fe (III)-reduction experiments were performed in both growth and non-growth media with two types of bacteria: mesophilic (*Shewanella putrefaciens* CN32) and thermophilic (*Thermus scotoductus* SA-01). Reductive dissolution of NAu-2 was observed and the formation of illite in treatment with thermophilic SA-01 was indicated by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). A basic pH (8.4) and high temperature (65°C) were the most favorable conditions for the formation of illite. A long incubation time was also found to enhance the formation of illite. K-nontronite (non-permanent fixation of K) was also detected and differentiated from the discrete illite in the XRD profiles. These results collectively suggested that the formation of illite associated with the biologically catalyzed smectite-to-illite reaction pathway may bypass the prolonged time and high temperature required for the S-I reaction in the absence of microbial activity.

Solar noble gases in Tagish Lake

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Tagish Lake fell in January 2000 [1] and is an ungrouped C2 meteorite and a 'breccia at all scales' [2]. Originally two different lithologies, a carbonate-rich one and a carbonate-poor one [2] were recognized, but additional work has revealed that there are even more distinct lithologies [3-5].

Analysis of the carbonate-rich lithology by [6] found abundant primordial noble gas, but solar noble gases were absent. A similar result was obtained by [7] in the analysis of a 'whole-rock' sample. Here we report noble gas data for a carbonate-poor sample of Tagish Lake, which, besides the primordial noble gases contains abundant solar gas.

We analyzed two samples. A smaller sample (#1; 20.2 mg) was heated in three temperature steps (600, 1000, 1800 °C), while a larger sample (#2; 93.9 mg) was heated in 200 °C increments from 400 °C to 1800 °C. Results for He, Ne and Ar are summarized in the Table below. Primordial Kr and Xe were also found at typical abundance levels relative to Ar (³⁶Ar/⁸⁴Kr/¹³²Xe ~ 80/0.85/1).

#	³ He	⁴ He	²² Ne	20/22	21/22	³⁶ Ar
1	5.99	16774	7.77	10.12	0.0851	90.3
2	8.35	22745	11.45	10.42	0.0853	96.4

Based on the presence of texturally and mineralogically distinct clasts, Nakamura *et al.* [6] concluded that the carbonate-rich lithology they studied is a breccia, however distinct from an asteroidal regolith breccia which would be characterized by the presence of solar noble gases. Our results indicate that there are other lithologies of Tagish Lake that in fact show solar wind gases. This and also the difference in cosmogenic ²¹Ne (in 10⁻⁸ cc/g units: 0.46 and 0.64 in our samples vs. 0.114 in [6]) indicate that different lithologies / clasts of Tagish Lake may have experienced quite different irradiation histories.

[1] Brown *et al.* (2000) *Science* **290**, 320–325. [2] Zolensky *et al.* (2002) *MAPS* **37**, 737–761. [3] Blinova *et al.* (2009) *LPSC XL*, #2039. [4] DeGregorio *et al.* (2010) *MAPS* **45**, A69. [5] Izawa *et al.* (2010) *MAPS* **45**, 675–698. [6] Nakamura *et al.* (2003) *EPSL* **207**, 83–101. [7] Grady *et al.* (2001) *MAPS* **36**, A71-A72.

Investigation the use of ozonation column for phenol removal

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The phenol and this compound are highly toxic and carcinogenic. This pollutant can be observed in the effluents of many industries such as petroleum refining, coal tar distillation and coke in steel mills [1-3]. Advanced oxidation specific ozonation was considered for water treatment as the potential research interest in recent years. Ozonation has a high capacity and suitable for remove phenol. Effective factors were evaluated initial phenol concentration, pH, H₂O₂ volume and Duration ozonation. The results of ozonation were shown that the percentage removal of phenol was related to time. Increased phenol concentration decrease phenol removal rate so that maximum of the percentage removal was obtained for 100, 200 and 300 ppm phenol respectively after 20, 35 and 55 min (Figure 1). The experiments were carried out in pH of 2, 4, 7 and 9. The results were illustrated in table 1.

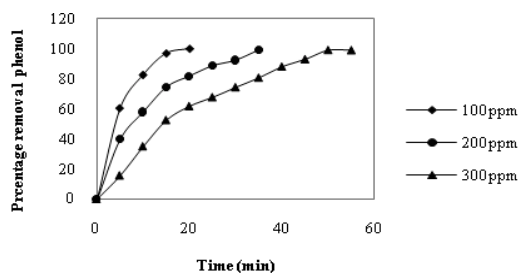


Figure 1: Effect of initial phenol concentration on removal

pH	2	4	7	9
Percentage removal 10 min (%)	55.18	65.12	70	95.3

Table 1: Effect of pH on phenol removal after 10 min

The most advantages of this study were the design of ozonation column and using a ozone diffuser that led to increase the percentage phenol removal in the shortest time possible. The optimum pH was 9 for remove phenol from wastewater and also increased H₂O₂ had little effect on removal.

[1] Moussavi *et al.* (2009) *J.Hazard. Mater.* **171**, 175–181.

Venting history and accumulation rates of hydrothermal sulfide, Endeavour Segment, Juan de Fuca Ridge

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Active hydrothermal systems on the ocean floor provide modern analogues for the formation of ancient VMS deposits. Seafloor hydrothermal processes are also an important mechanism for the transfer of heat and chemicals between the underlying crust and oceans. However, the rates at which these processes occur remain poorly constrained.

Here, we present radioisotope ages and volume estimates of hydrothermal sulfides from the Endeavour Segment, an intermediate rate ocean spreading center along the Juan de Fuca Ridge that hosts 5 active high-temperature vent fields. The ridge is currently undergoing a period of tectonic extension and volcanic quiescence. A suite of 43 sulfide samples, collected by manned submersible from the active fields and extinct/inactive sites, have been dated using ²²⁶Ra/Ba ratios from hydrothermal barite that precipitates along with sulfide minerals. Radium-226 has a half-life of 1,600 years, making it an ideal chronometer for samples younger than ~20, 000 years. Results indicate that venting within the current axial valley of the Endeavour segment was initiated at least 2, 500 years ago. Venting within the Main Endeavour Field, the largest field by area, has been continuous for this period of time.

Using a GIS-based volume calculator developed at MBARI, the total volume of hydrothermal sulfide (including active and inactive/extinct structures) is determined from high-resolution bathymetry of the entire ridge segment. By combining volume data with the age of venting at Endeavour, the mass accumulation rates of sulfide can be determined at the segment scale. These results can be used to calibrate the efficiency of sulfide deposition from hydrothermal vents, and provide a time-integrated history of heat, fluid and chemical fluxes at the ridge-segment scale. The comparison of time-integrated rates with real-time estimates, based on fluid and chemical fluxes, as well as heat flow measurements, allow for an estimate of the episodicity of venting at Endeavour.

Porosity evolution, fracturing and Liesegang-banding during spheroidal weathering

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A 10-meter thick andesitic sill intrusion from the Neuquen Basin, Argentina, shows spectacular examples of spheroidal weathering and Liesegang banding. The Liesegang patterns demonstrate how andesite blocks, initially cut out by a pre-weathering joint set, are subdivided by fractures forming during the spheroidal weathering process. The stresses causing fracturing originate from the growth of ferrihydrite and calcite in the pore space of the andesite, partly at the expense of original ilmenite, amphibole, and plagioclase. Fresh andesite has a porosity of ca. 8%. The porosity evolution and fracture formation during progressive weathering has been characterized in 3D by X-ray computed tomography (CT). The extent of pore filling increases with pore-size. Pores > 10⁶ μm³ are almost completely filled, whereas pores < 10³ μm³ are < 50% filled. More than 85% of the pore volume is comprised of pores < 10³ μm³, and thus the overall porosity is only slightly reduced during weathering. The fracturing associated with spheroidal weathering is caused by growth in pores comprising the largest 10% of the total porosity. We suggest that variation in growth rate with pores size is controlled by more effective transport of externally derived components to the larger pores. Models for diffusive transport in a porous rock with a pore size distribution similar to the observed will be presented, along with a fracturing model where stresses are generated by growth in pores.

**New isotopic constraints on
Amsterdam-St. Paul hotspot activity:
Evidence for a deep-seated mantle
plume and implications for the
DUPAL anomaly origin**

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The Amsterdam-St Paul oceanic plateau (ASP) results from the interaction between the ASP hotspot and the Southeast Indian ridge. A volcanic chain, named the chain of the dead Poets (CDP), lies to its northward tip and is related to the hotspot intraplate activity.

The ASP plateau and CDP study reveals that ASP plume composition comes from oceanic crust and pelagic sediments recycled in the mantle through a 1.5 Ga subduction process. The ASP plateau lavas have a composition (major and trace elements and Sr-Nd-Pb-Hf isotopes) reflecting the interaction between ASP plume and the Indian MORB mantle, with some clear DUPAL input [1].

The Indian upper mantle below ASP plateau is heterogeneous and made of a depleted mantle with lower continental crust strips probably delaminated during the Gondwana break-up. The lower continental crust is one of the possible reservoirs for the DUPAL anomaly origin [2-3-4-5] and our data support it. The three endmembers involved (plume, upper mantle and lower continental crust) and their mixing in different proportions enhances an important geochemical variability in the plateau lavas.

[1] Hart, (1984) *Nature* **309**, 753–757. [2] Arndt, Goldstein, (1989) *Tectonophysics* **161**, 201–212. [3] Escrig, Capmas, Dupré, Allègre, (2004) *Nature* **431**, 59–63. [4] Hanan, Blichert-Toft, Pyle, Christie, (2004) *Nature* **432**, 91–94. [5] Meyzen, Ludden, Humler, Luais, Toplis, Mével, Storey, (2005) *Geochem. Geophys. Geosyst.* **6**, Q11K11

**Development of an active mine water
treatment technology by use of
schwertmannite**

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As a residual of microbial ferrous iron oxidation, large amounts of schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$) were produced in a pilot plant for lignite mine water treatment in Tzschelln (Lusatia, Germany). The secondary mineral has excellent properties for removal of arsenic and other oxoanions from mine water and rapidly transforms into ferric hydroxides of high specific surface area once exposed to water containing at least some alkalinity. Therefore, the research project SURFTRAP was carried out to investigate the applicability of schwertmannite for the treatment of ground- and surface water contaminated with arsenic.

Following to fundamental, hydrochemical and structural investigations in the laboratory, a pilot scale test was performed in the bypass of an active water treatment plant for contaminated flooding water from uranium ore mining. About 25 mg Fe/L as schwertmannite were necessary to undershoot the governmental described effluent limits (0.3 mg As/L and 0.5 mg U/L). The costs of the higher demand of schwertmannite compared to the conventional FeCl_3 additon (10 mg Fe/L) could be compensated by a reduction of lime milk requirement of about 25%.

Furthermore, dumping experiments with arsenic-loaded schwertmannite-sludges were performed. A discontinuous irrigation scenario and a continuous groundwater equilibration scenario was investigated. After one year, no significant arsenic release was observed.

Pb-Sr-Nd-Hf isotope variations of megacrysts from Mesozoic Southern African kimberlites reflect mixing of HIMU melts with deep lithosphere

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Clinopyroxene (cpx) megacrysts are abundant in southern African kimberlites and most have compositions that are not in equilibrium with normal mantle peridotite. Cpx megacrysts constitute a major part of the Cr-poor megacryst fractionation sequence. Although much of their major element variation is attributable to simple fractional crystallization, deflection of the fractionation trends in many cases toward Cr- and Mg-rich compositions suggests that crystallizing megacryst parental magmas are not closed systems. We present Pb-Sr-Nd-Hf isotope data for cpx megacryst samples at regular intervals along evolution paths. The two localities we have examined in detail thus far, Pofadder and Monastery, display illuminating similarities and differences. Mg- and Cr-rich compositions dominate the cpx megacryst population at Pofadder, with only a minority of Cr-poor varieties. These megacrysts describe wide variations in all isotope systems (e.g. $^{206}\text{Pb}/^{204}\text{Pb} = 18.3$ to 19.6) with the Cr-poor megacrysts having the most radiogenic Pb (although with lower $\Delta 7/4$ and $\Delta 8/4$), Nd and Hf isotope ratios. At Monastery, Cr-poor varieties dominate the cpx megacryst assemblage, with a small population of only moderately Cr-rich megacrysts. Here, isotope ratios display a much smaller variation (e.g. $^{206}\text{Pb}/^{204}\text{Pb} = 20.3$ to 20.8) and encompass HIMU compositions comparable to the most extreme OIB at St. Helena. Pb becomes progressively less radiogenic as Cr# gradually drops with decreasing Mg#, and this progression continues as the evolution path is deflected toward higher Cr# and mildly increased Mg#. Our isotope data are consistent with an increasing degree of mixing between megacryst parental magmas having HIMU isotopic characteristics and deep lithospheric peridotite (having relatively unradiogenic $^{206}\text{Pb}/^{204}\text{Pb}$, Nd and Hf) with increasing magma evolution, the extent of assimilation appearing to be much greater at Pofadder than at Monastery. The nearly monotonic changes in the isotope ratios of cpx megacrysts from Cr-poor to Cr-rich compositions at these localities confirms that the two suites are petrogenetically related. Moreover, such mixing may be partly responsible for the lack of strong HIMU compositions directly observed in southern African kimberlites

Geochronological, geochemical and growth constrains of Alpine clefts from U-Th-Pb in monazite

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Monazite is a powerful U-Th-Pb chronometer of geological processes. Although conditions that drive its dissolution and precipitation remain unclear, monazite occasionally occurs in hydrothermal veins. Recent studies showed that hydrothermal monazite is successful to date mineralization. The originality of the present work is to evaluate if compositional and isotopic signature of monazite can record the geochemical environment and duration of rock-fluid interaction.

For this study, the selected monazite crystals satisfy two criteria: they are geologically young to ensure a Ma-resolution in age, and large enough (~mm-sized) to detect an age evolution over a grain profile. Studied monazite come from two distinct Alpine clefts from Central Alps (Griessental and Blaubeurg, Switzerland). U-Th-Pb isotopic data were measured using ion microprobe.

In the two hydrothermal monazite crystals, U-Th-Pb isotopic signature gives indications about the ages, duration, $f\text{O}_2$ and geochemical environment (close vs open system) of the mineralization. Geochronologically, the Th-Pb age is preferred to the U-Pb age (s), because of (1) the unusually low U/Th contents, (2) significant contribution of common Pb and (3) ^{206}Pb excess in the Griessental crystal, related to significant incorporation of ^{230}Th . Blaubeurg and Griessental crystals show similar Th-Pb ages ~12 Ma, with no significant variations. However, one younger analysis point (~10 Ma) suggests possible crystallization over 2 Ma in the Blaubeurg crystal. Compositionally, both crystals show unusually high Th/U values, indicating oxidizing conditions and dominant hexavalent U. Blaubeurg monazite is rather homogeneous displaying some sector zoning. The Griessental crystal has a rim with higher Th/U and ^{206}Pb excess (up to 80% of the ^{206}Pb) than in its core. This zoning is coherent with a two-stage crystallisation in a closed system. While ^{230}Th was in disequilibrium with the U-series when the core precipitates, the fluid had time to reach equilibrium when the rim crystallized.

Nature, origin and causes of Jurassic felsic igneous activity in the Victory Glacier area (Eastern Graham Land)

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Geochemical signatures of felsic igneous rocks (biotite granites and rhyolite dykes) from the Victory Glacier area (eastern Graham Land, Antarctic Peninsula) are mutually indistinguishable, corresponding to high-K calc-alkaline, subaluminous to slightly peraluminous rocks. The NMORB-normalized spiderplots show strong LILE/HFSE enrichment typical of magmas generated at active continental margins or having originated by anatexis of mature continental crust. Characteristic are also fractionated chondrite-normalized REE patterns with deep negative Eu anomalies. The Sr–Nd isotopic signatures are those of fairly evolved crust ($^{87}\text{Sr}/^{86}\text{Sr}_{175} = 0.7084\text{--}0.7107$, $\epsilon^{175}_{\text{Nd}} = -4.4$ to -4.8). Taken together, the felsic rocks most likely originated from highly differentiated magmas derived by low-P (residue lacking Grt), low-T (Mnz and Zrn saturation temperatures ~ 770 °C) anatexis of metapsammities or orthogneisses. The widespread crustal anatexis took place within attenuated crust, as a part of the Chon Aike silicic large igneous province [1] magmatism.

New U–Pb Zrn dating shows that the Jurassic magmatic flare-up was rather short-lived (Toarcian–Aalenian). The two recognized Bt granite generations ($\sim 185/\sim 166$ Ma) both pre- and post-dated the rhyolitic volcanism ($\sim 174\text{--}179$ Ma).

Field relationships indicate that the rhyolite dykes were emplaced in a biaxial extension deformation regime. The appropriate tectonic setting was either rifting accompanying mantle-plume-assisted Gondwana break-up [2] or extension behind the emerging Antarctic Peninsula arc [3]. The two scenarios do not have to be mutually exclusive, though [1, 4].

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A physiochemical analysis of the mechanisms for transport and retention of Technetium (^{99}Tc) in unsaturated Hanford sediments

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The transport of technetium (^{99}Tc) is of interest due to the potential for human exposure and impact on ecosystems. Technetium has been released to the environment predominantly through nuclear fuel processing; as a result, further spreading of ^{99}Tc is a concern at DOE sites across the US. Specifically, technetium is a contaminant of concern at the Hanford Site in southeastern Washington, due to the magnitude of material that was disposed. The current body of work conducted on ^{99}Tc has provided a wealth of information regarding the redox relationships, sorption, solubility, and stability of the mineral phases [1], however little work has been conducted on the transport of technetium under vadose zone conditions.

The current conceptual model for technetium transport in the Hanford deep vadose zone is driven by two dominant hypotheses. The first component, proposes technetium movement is dominated by anisotropy and capillary forces; with the mobile technetium spreading laterally across higher conductivity saturated zones and being resisted by low saturation high conductivity zones. Within these regions technetium transport is considered highly dependent on the unsaturated hydraulic conductivity and capillary pressure. Thus, understanding saturation dependent technetium transport is critical for estimating the vertical fluxes of technetium and predictive modelling. The second premise assumes that technetium is in the form of the oxic pertechnetate species. Using an integrated testing approach we examined the mechanisms for physical and chemical retention and transport of technetium in unsaturated sediments. By employing transport and breakthrough curve analysis as well as pore water and sequential extractions, we evaluated transport behaviour, technetium mineral association, and technetium leachability with regard to pore size distribution.

[1] Artinger *et al.* 2003; Beals and Hayes, 1995; Cui and Eriksen, 1996b; Gu and Schulz, 1991; Jaisi *et al.* 2009; Keith-Roach *et al.* 2003; Kumar *et al.* 2007.

Pushing the limits of AMS measurements of cosmogenic radioisotopes in natural systems

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Pushing the detection limits of cosmogenic radioisotopes using Accelerator Mass Spectrometry (AMS) techniques will be extremely advantageous to the field of earth sciences. In the late 1970's research in earth sciences was revolutionized by the use of AMS to achieve isotopic levels many orders of magnitude lower than conventional mass spectrometers. In earth sciences AMS techniques are most commonly employed for the measurement of cosmogenic radioisotopes. These isotopes are most useful for quantifying processes at Earth's surface. At the Holifield Radioactive Ion Beam Facility (HRIBF) we have exceptional capabilities owing to the unique set up including the highest operating voltage electrostatic accelerator in the world, the 25-MV Tandem, as well as unique beam transport components and peripheral equipment. This system allows for the detection of extremely rare isotopes and effectively remove isobar interferences. Recent measurements on ³⁶Cl/Cl ratios within seawater samples have shown that the levels of detection can be pushed as far as 10⁻¹⁶ [1]. Recent developments of new AMS methods such as photodetachments of negative ions may allow us to push the limits even further and increase the range of radioisotopes that can be detected [2]. I will describe an on-going research program at HRIBF that includes identifying natural systems where this extra sensitivity could make a difference. Measurements at the limit of sensitivity will contribute to constrain the predictions from cosmogenic production models at Earth's surface.

[1] A. Galindo-Uribarri *et al.* (2007) *Nucl. Instr. Meth. B* **259**, 123. [2] A. Galindo-Uribarri *et al.* (2010) *Nucl. Instr. Meth. B* **268**, 834.

Linking geochemistry to microbial community structure and function in sulfidic geothermal systems of Yellowstone National Park

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Analysis of metagenome sequence from high-temperature microbial communities in Yellowstone National Park (YNP) suggests the importance of heterotrophic, S-respiring crenarchaeal populations in sub-oxic sulfidic sediments. The primary goal of this study was to determine the role of Thermoproteales and Desulfurococcales populations in S and C cycling in these communities using both molecular and culture methods. Metagenome sequence was obtained from three sub-oxic, elemental S-dominated hot springs in YNP: Monarch Geyser (80° C, pH 4), Cistern Spr. (CS; 76° C, pH 5) and Joseph's Coat HS (JCHS; 80° C, pH 6). Major sequence assemblies from these sites resulted in nearly complete consensus genomes of *Acidilobus*, *Vulcanisaeta* and *Caldivirga*-like organisms in all sites, *Thermoproteus/Pyrobaculum* spp. in JCHS and CS, and two different Sulfolobales phylotypes in CS. Several enzymes and transporters involved in protein, carbohydrate, and lipid catabolism were identified. The predominant community members all contain bd-ubiquinol oxidase genes and lack any evidence for heme-copper oxidases often associated with aerobic respiration. The expression of genes involved in anaerobic respiration, including novel S reductases in the dimethylsulfoxide (DMSO) molybdopterin family, NAD (P)H:S⁰ oxidoreductases, and nitric oxide reductases, was studied using RT-PCR to estimate the activity of these processes in each habitat. Results from molecular analyses of field samples were compared to controlled experiments using a *Pyrobaculum* sp. isolated from JCHS that is capable of growing anaerobically on S⁰, using yeast extract as a C and energy source. This organism contains a novel DMSO reductase, highly related to gene sequences identified in the JCHS metagenome. The effect of S⁰ particle size on microbial growth was evaluated in concert with the expression of novel DMSO reductases. These data provide insight regarding the structure and function of high-temperature microbial communities, and the role of specific phylotypes in S and C cycling in sub-oxic, sulfidic geothermal systems.

Chemical speciation of airborne mineral dust in the Middle East

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Background

On July 8, 1997, the U.S. Environmental Protection Agency (EPA) promulgated a new national ambient air quality standard (NAAQS) for particulate matter with an aerodynamic diameter less than 2.5 μm (PM_{2.5}). In response to the new NAAQS, EPA established two networks: the larger network monitors total mass to assess compliance with the standard. The second, smaller network, the PM_{2.5} Chemical Speciation Network (CSN) provides data to support attainment activities, and supplies a broad-based dataset to support human health studies and other research. RTI International has provided analytical services and other support to the chemical speciation network since early 2000.

Project Description

Desert Research Institute (DRI) contracted with RTI to provide analytical services for the U.S. Army's Enhanced Particulate Matter Surveillance Program (EPMSP), which began sampling in late 2006. The primary objective of EPMSP was to gather information on the chemical and physical properties of ambient PM in the Middle East. Ambient air samples were collected over a period of approximately one year at 15 sites, which included Djibouti, Afghanistan, Qatar, United Arab Emirates, Iraq, and Kuwait. Three particulate size fractions were sampled: PM_{2.5}, total suspended particulates (TSP), and particulate matter less than 10 μm (PM₁₀). Teflon, nylon, and quartz filters were used for sampling, and all filters were subsequently analyzed by RTI. Analyses included: trace elements (by X-ray Fluorescence Spectroscopy), anions and cations (by ion chromatography), total mass (by gravimetry), and elemental, organic, and carbonate carbon (by Thermal-Optical Transmittance).

Discussion

Because of the high levels of mineral dust found in the deserts of the Middle East, the levels of crustal elements found in the EPMSP samples were significantly higher than in CSN samples from the U.S., which posed some analytical challenges that will be discussed in this presentation.

Trace element geochemistry of soils in fluoride-rich shallow groundwater sites in Sri Lanka

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Higher groundwater fluoride is a controversial issue in dry zone of Sri Lanka. This study described the geochemistry of residual soil from higher (< 8 mg/L) and lower (< 1 mg/L) water fluoride sites in dry zone to identify possible sources for fluoride. Twenty two major and trace elements have been determined for seventy four soil samples by means of X-ray fluorescence. Results denote that soil fluoride is lower than upper continental crust and basement rocks in both higher (<411 mg/kg) and lower (<277 mg/kg) water fluoride sites. Negative linear correlation exists between fluoride in the soil and the water suggested that fluoride readily leaching to water rather than retaining in soils due to unconsolidated sandy clay loam texture. Weathering of heavy minerals such as zirconium, apatite, fluorite, monazite and garnet are the main source for the soil in high water fluoride area. Consequently, stable extent of Zr, Nb and Th and depletion of F together with CaO and P₂O₅ than basement is occurred, hence loss of CaO provides favourable condition to leach F to water. Conversely, lower water fluoride area soils show enrichment of TiO₂, Fe₂O₃, MnO, Cr, V and Sc denote the weathering of biotite, hornblende, garnet and pyroxenes in the basement. Primary minerals present in that soil is the main cause for the enrichment of those elements. Further, fluoride levels in the soil and subsequently in water show close link with magmatic differentiations along the geological formations. Thus soil geochemistry evident that meta-igneous rocks of the higher water fluoride area may have associate with a fluoride rich residual melt while lower water fluoride area associate with acidic meta-igneous rocks with concordant meta-sedimentary rocks.

Transfer of uranium isotopes, thorium and their decay products to edible plants

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Some of the primordial radionuclides (uranium, thorium and their decay products) are the main source of both external and internal radiation for humans. They can be incorporated metabolically into plants and can be transferred to animals and humans via the foodchain. However, there is a lack of data concerning the Earth crust derived actinides measured in edible plants. Furthermore their main sources as well as their mechanisms of transfer are still misunderstood. Indeed, whereas radionuclides such as uranium and radium would be transferred by root uptake, others radioelements like ²¹⁰Po and ²¹⁰Pb are preferentially carried by atmospheric particles. The aim of this work is firstly to understand the differences in activity between various plants species. The appreciation of the equilibriums and the disequilibriums between radionuclides in the decay series as well as the uptake of radionuclides by roots and the inputs by the atmosphere and irrigation should be taken into account to clarify the transfer mechanisms responsible of these differences. Secondly, the objective consists in studying the variability of natural radioactivity in edible plants, according to uranium content in soils from various areas with different geological characteristic and anthropic influence like the nuclear fuel cycle which may enhance the activity in local foodstuffs.

Fluid-mobile element enrichment in mantle wedge of subduction zones

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Our previous work has shown that supra-subduction zone ophiolites, which form in the mantle wedge of nascent subduction zones, preserve mantle lithologies that formed in response to hydrous melting and represent the refractory residuum of that process [1-3]. In this study we document the a new algorithm for using fluid-mobile element (FME) concentrations in unaltered residual pyroxenes to calculate the composition and flux of slab-derived fluids in the mantle wedge during melting.

We use high-precision laser ablation ICP-MS analyses (Element 2 ICP-MS with 213 nm laser) of relic pyroxenes in supra-subduction zone peridotites for B, Be, Rb, Th, Ba, Li, and Pb – analyzed in conjunction with a suite of non-fluid mobile elements including the REE and high-field strength elements, which are used to assess melt extraction and melt percolation. Pyroxenes in all SSZ ophiolite samples display enrichments in the FME relative to depleted MORB mantle. In contrast, melting models based on the MREE-HREE and HFS elements show that the FME should have concentrations that are effectively zero after significant melting. We derive an algorithm may be used to calculate the FME:

$$C_{wr,add} = [C_{cpx-obs} / \{ [D_{cpx} / (D_{bulk} - PF)] * [1 - (PF/D_{bulk})]^{(1/P)} \}] - [C_{0,wr}]$$

Where $C_{wr,add}$ = concentration of FME added to mantle wedge, $C_{cpx-obs}$ = observed pyroxene, D_{cpx} and D_{bulk} = mineral and bulk partition coefficients, P = melt proportion, and F = melt fraction.

Melt models require enormous fractions of FME if the peridotite and fluid are 'mixed' prior to melting. However, if the calculated fluid is added continuously so that it is in equilibrium with the observed refractory pyroxenes, fluid addition models provide reasonable results.

Our results show that high concentrations of fluid-mobile elements in supra-subduction peridotites can be attributed to a flux of aqueous fluid or fluid-rich melt phase derived from the subducting slab. Further, our calculated FME-enriched source yields model melts with the trace element signatures of the arc volcanics.

[1] Choi *et al.* 2008 *Cont Min Pet* **155**, 551–576. [2] Choi *et al.* 2008 *Geology* **36**, 595–598. [3] Jean *et al.* 2010 *Cont Min Pet* **159**, 113–136.

Raman spectroscopic identification of evaporitic minerals and biomarkers using miniaturised portable devices

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Raman spectroscopy for exobiological applications

It is advocated that in the frame of forthcoming probes planned within future exobiological missions on Mars, Raman spectroscopy will play an important role. It is planned to use this non-destructive tool to identify both minerals and potential organic compounds – possible biomarkers of preexisting life. In this work, minerals from four groups (halides, sulphates, carbonates and borates), examples of pigments known from bacteria, as well as selected osmotic biochemicals (betaine, ectoine), were investigated to estimate the potential of miniaturised spectrometers to work under complex Earth conditions to detect these compounds. Raman spectra were obtained outdoors using a portable Raman spectrometer (DeltaNu, Inspector Raman, excitation 785 nm). Collection specimens and reference compounds were investigated, as well as white evaporitic crusts from two dry evaporitic lakes (Bristol Lake, Owens Lake, California, U.S.A.) and saltern evaporation ponds (Eilat, Israel).

Results

Generally speaking, excellent identification of minerals and associated biomaterials through their Raman band positions was achieved on mineralogical specimens from collections. Good results were obtained using the portable spectrometer outdoors on native white evaporitic crusts under ambient atmospheric conditions. Shielding of the measurement area against insolation was nevertheless necessary. Although the recording of weaker Raman features was sometimes problematic, this did not compromise the precise identification of the mineral concerned. Raman spectra of investigated pigments and halophile osmotic compounds obtained permit their reliable identification as well.

Chalcophile element systematics in the North West Lau backarc basin

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The Lau Backarc Basin hosts numerous individual spreading centers, including the 70 km-long Northwest Lau Spreading Center (NWLSC) located ~500km west of the northern Tonga Arc volcanic front. Submarine volcanic glasses with from 9 to 2 wt.% MgO (49-62 wt.% SiO₂) were recovered from the NWLSC. These samples show no evidence of a subducted slab component. There is no indication of S loss by degassing. Fractional crystallization of olivine and clinopyroxene drives the liquid to high FeO* with decreasing MgO until the appearance of magnetite on the liquidus at ~4 wt.% MgO. S parallels FeO* but the S levels are initially below those of sulfide-saturated MORB, indicating undersaturation in sulfide. Consequently Cu, Se and Ag also initially increase with decreasing MgO. The apogee in Cu, Ag and Se contents, attributable to sulfide saturation, is at ~5.5 wt.% MgO, notably earlier than the maximum in FeO* and S. Because S simply tracks FeO* at sulfide saturation, the Cu-Ag-Se trend reveals the onset of sulfide saturation better than S itself. The behaviour of Cu, Se and Ag in the basaltic to andesitic suite from the NWLSC is intermediate between MORB and oxidised backarc basin magmas; it contrasts with that from the Pual Ridge back arc basin by reaching sulfide saturation prior to the onset of magnetite fractionation. Therefore, chalcophile elements in the NWLSC are removed by continuous pyrrhotite fractionation whereas the more oxidised Pual Ridge magma fractionates to very high chalcophile element abundances before massive precipitation of Cu-Ag (and Au) sulfide at the magnetite crisis.

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Characterization of magma from inclusions in zircon: Apatite and biotite work well, feldspar less so

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Detrital zircon grains are frequently employed to decipher sediment provenances and crustal evolution throughout Earth history, and they provide unique evidence of Hadean crust-mantle differentiation. However, interpretation of detrital zircon is hampered by the remarkably restricted range of geochemical characteristics of zircon derived from a range of igneous source rocks. Mineral inclusions in zircon are an underexploited resource and provide valuable additional petrologic information on the condition under which zircon crystallised. Zircon grains from a range of plutonic rocks (diorite-monzonite-granite sequence) contain inclusions of apatite and mafic phases (biotite, amphibole, pyroxenes) which accurately reflect the chemical compositions of the equivalent phases in the matrix of the host rocks. Chemical characteristics of the inclusions, such as Mg/Fe ratios of mafic phases, and Sr abundances in apatite, correlate well with the compositions of the whole rocks. High concentrations of Y₂O₃ (>0.4 wt%) and low concentrations of SrO (<0.02 wt%) in apatite inclusions in zircon are diagnostic of evolved, felsic granitoid host rocks. In strong contrast, the relative abundances and compositions of plagioclase and alkali feldspar inclusions in zircon are decoupled from the composition of the whole rock, and are generally indicative of chemically evolved, granitic melts, regardless of the bulk rock composition. This is best explained by the late crystallization of zircon relative to the bulk of the feldspars.

We conclude that inclusions of apatite and mafic phases in zircon constrain the potential source rocks of detrital zircon, whereas feldspar inclusions do not. This ability to differentiate between grains from primitive and evolved sources has important applications to the interpretation of Hadean zircons.

Secular trends in granite zircon εHf-δ¹⁸O, Australian Tasmanides

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The possible role of arc/back-arc accretionary processes in generating continental crust has recently been highlighted [1]. In this context, it has been argued that the Phanerozoic Tasmanides (~3000 x 6000 km) comprising the eastern third of the Australian continent formed during repeated opening and closing of sediment-filled back-arc basins triggered by alternating slab rollback and advances in a long-lived Cambrian to Triassic subduction system [2]. Kemp *et al.* [3] attempted to correlate additions of newly formed juvenile crust to the Tasmanide igneous rocks with the pattern of deformational/tectonic events during three orogenies (Delamerian, Lachlan, New England) using isotope signatures (whole rock Nd, zircon U/Pb, Hf and O). They proposed S-type granite emplacement in thickened crust followed by increasing juvenile contributions during back-arc rifting. The limited data set did not fully define the long-term Tasmanide isotopic trend, however, and few data represented the key Carboniferous event between the main crust forming episodes in the Lachlan (LFB) and New England (NEO) orogens.

New zircon U-Pb, Hf and O isotopic data from Carboniferous-Early Triassic granites in the LFB and NEO have been used to test the Kemp *et al.* [3] tectonic model. The I-type LFB Carboniferous granites show a trend from juvenile to more crustal (higher) δ¹⁸O_{Zrn} with time, but a step from strongly to weakly positive εHf (t). Permian S-type granites of the NEO have very high, crustal δ¹⁸O_{Zrn}, but uniformly moderately positive εHf (t). Most analysed NEO I-type granites have moderate δ¹⁸O_{Zrn}, except for the oldest, in which the range of δ¹⁸O_{Zrn} is similar to that in the LFB S-types. All have moderately to strongly positive εHf (t).

The zircon Hf and O isotopic compositions in the post-Devonian granites of the LFB and NEO are decoupled. Further, emplacement of the NEO S-type granites did not coincide with any recognised deformation episode. These features are not consistent with current models of arc/back-arc accretion.

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Lead isotopic compositions for Pb-Zn deposits in the Eastern South Korea

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In this paper, the lead isotopic compositions of galena, collected from 15 lead-zinc deposits in the eastern part of South Korea were analyzed, mainly aiming at understanding the regional variation and the geochemical evolution of Pb isotopic composition of lead-zinc deposits in Korea.

For 9 lead-zinc deposits in the Ogcheon system and the Yeongnam massif, Pb isotopic compositions of galena are ranging 18.562-19.784 for ²⁰⁶Pb/²⁰⁴Pb, 15.729-15.934 for ²⁰⁷Pb/²⁰⁴Pb, and 38.849-39.859 for ²⁰⁸Pb/²⁰⁴Pb.

In contrast, for galena samples collected from 6 lead-zinc deposits in Gyeongsang basin, the lead isotopic composition varies in a relatively small range; those isotopic compositions of ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb are in the range of 18.265-18.441, 15.581-15.726 and 38.332-38.993, respectively, which are slightly lower than those observed in the Gyeongsang basin.

Based on our observations, it seems that lead isotopic compositions in Korea can be classified according to the tectonic boundary between the Gyeongsang basin and the Yeongnam massif. Also, it appears that Pb for lead-zinc deposits in the Ogcheon system and the Yeongnam massif seems to have been originated from upper crustal materials of old continental, because they fit well onto the general trend of lead isotopic compositions of Precambrian basement rocks in South Korea.

Ni and Cr speciation in soils formed on ultramafic rocks from Barberton Greenstone Belt (South Africa)

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Five soil samples were collected by Jolanta Mesjasz-Przybyłowicz (from the depth of about 10 cm) near the Agnes Mine in Mpumalanga Province, the Republic of South Africa. Soils are formed on amphibole-talc shists and serpentinites of Onverwacht Group in Barberton Greenstone Belt. Soils are characterised by mean Mg/Ca ratio 4, 27 and mean pH_{H2O} value 5, 43 [1].

Soil samples and the bedrock fragments were analyzed using optical microscope, SEM EDS and X-ray diffraction. Seven-step sequential extraction (exchangeable ions, carbonates, manganese oxides, amorphous iron oxides and hydroxides, crystalline iron oxides, organic matter and sulfurs, residual fraction) was executed on 4 soil samples. Chemical composition of soils and extracts was determined using IPC MS and ICP AES.

Soils are composed mainly of amphibole, talc, serpentine, chlorite, quartz and various clay minerals. According to EDS measurements of weathered rock fragments from soils, the most important Ni and Cr bearing phases are rarely occurring Mn-oxides, Fe-oxyhydroxides and commonly occurring various phyllosilicates. Mean and maximal values are listed in Table 1.

wt. %	Phyllosilicates		Fe-oxyhydroxides		Mn-oxides	
	NiO	Cr ₂ O ₃	NiO	Cr ₂ O ₃	NiO	Cr ₂ O ₃
Mean	0,12	0,21	0,43	1,76	9,69	0,05
SD	0,58	1,11	1,25	2,7	4,28	0,15
Max.	12,53	3,85	6,81	16,74	17,74	0,42

Table 1: Mean and maximal concentrations of NiO and Cr₂O₃ (wt.%; EDS results) in weathered rock fragments

Sequential extraction experiment results agree with EDS studies. About 50% of Ni and Cr are bound to residual phases which are mainly silicates. Almost 50% of Cr is accumulated in crystalline Fe-oxides. Very important Ni containing phases are crystalline and amorphous Fe-oxides (respectively 27% and 8%) and to a lesser amount Mn-oxides (5%).

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Changes in microbial community structure associated with dynamics in oxygen supply at the Crimean shelf of the Black Sea

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Today's rapid global warming of oceans together with eutrophication appears to promote a deoxygenation of some of the world's water bodies [1, 2], which eventually leads to hypoxia and even anoxia in regions of low oxygen supplies. With less than 60 μM oxygen most animals are negatively impacted and microorganisms dominate benthic energy fluxes [3]. As a result, it can be expected that in zones with oxygen dynamics around this tipping point benthic and microbial community structure will vary considerably in space and time, with repercussions on the flux of energy and matter through the ecosystem. Here we present effects of varying hypoxic conditions on benthic microbial communities. Sediments from a series of transects across oxic to hypoxic conditions at the Crimean shelf of the Black Sea were analysed by community fingerprinting using ARISA (Automated Ribosomal Intergenic Spacer Analysis), in order to assess the connections between oxygen supply and benthic microbial community structure.

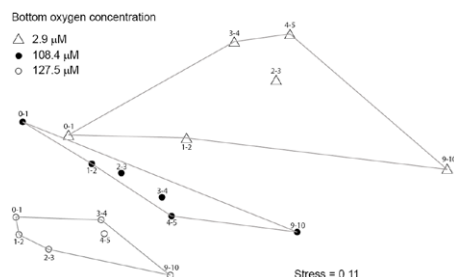


Figure 1: NMDS ordination plot (Bray-Curtis distance matrix) of ARISA profiles for the upper 10 cm layer sediment. Numbers represent each horizon sampled (cm).

Our data clearly exhibited a strong change in benthic bacterial community structure along a sampling transect including oxic, anoxic and highly dynamic hypoxic zones (Fig. 1), indicating an effect of temporal dynamics in oxygen supply at the microbial scale. This study is supported by the EU project HYPOX.

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Sulfur, carbon and nitrogen isotopic variation in the drinking water source of Beijing

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Samples of water, suspended particulate matter and sediments were collected in the drinking water source of northern Beijing and analyzed for sulphur, carbon and nitrogen isotopic compositions. The results showed that: (1) The ratios of sulphur isotope were between 4.9‰ and 10.7‰ in water samples; (2) The carbon and nitrogen isotopic ratios in suspended particulate matter were -29.34‰–25.91‰ and -0.96‰–6.73‰ in summer, and -30.75‰–25.75‰ and -0.83‰–9.67‰ in winter, respectively; (3) The sulphur, carbon and nitrogen isotopic ratios in surface sediments were -11.8‰–6.1‰, -27.25‰–21.58‰ and 1.32‰–6.74‰, respectively. The differences of sulphur isotopic compositions in surface sediments from different sampling sites show the differences in the sources of sulphur. The suspended particulate organic matter was derived mainly from SOM-C₃ and macrophyte in summer, while it was derived from SOM-C₃ and plankton in winter. Surface sedimentary organic matters were mainly derived from SOM-C₃. Nitrogen isotopic ratios reflected the combined results of materials source and it can be used to trace some special biogeochemical processes. This study reveals that the source of organic matter has a close relationship with the situation of soil erosion in the areas.

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Research on chronology and formation mechanism of Xiaorequanzi Cu-Zn field in Tianshan Orogenic Belt, Western China

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A large number of VHMS deposits have developed within Tianshan orogenic belt in western China, and Xiaorequanzi Cu-Zn field, consisting of several sulphide deposits, is more typical. There are three perspectives on the genesis of the deposit. First, according to the phenomena that intermediate-acid porphyry veins usually emerge near the ore body, the copper amount of porphyries is several times higher than the Clarke value of similar rocks, it is a porphyry copper deposit. Second, based on the features that the deposit occurs in the Xiaorequanzi volcanic rocks, ore body is layered and like-layered, it is a VHMS deposit. Third, on the basis of the traits that oxide ores in the surface and deep primary ores are more veins, it is volcanic hydrothermal-type deposit.

In order to identify the mineralization age and genesis of Xiaorequanzi Cu-Zn deposit, the metallogenetic and magmatic events in mining area were systematically researched by Rb-Sr isotopic geochronology. The whole-rock Rb-Sr isochron age of ore-bearing rocks, andesite, is 313Ma; the Rb-Sr isochron age of quartz fluid inclusion in copper-bearing quartz veinlets is 297Ma; the age of albite porphyry is 267Ma; the Rb-Sr isochron age of quartz fluid inclusion in stockwork copper ore, which formed in the period of magmatic hydrothermal, is 264 Ma. Isotopic dating results show that Xiaorequanzi Cu-Zn field belongs to the composite deposit, consisting of volcanic exhalation sedimentation and post-magmatic hydrothermal reworking. The mineralization should be divided into two phases: the main occurred in the late Carboniferous, 313~297Ma, which is consistent with the time of volcanic eruptions. Superimposed mineralization of the late magmatic hydrothermal occurs in the middle to late Permian, about 264Ma, which is roughly the same as the emplacement time of subvolcanic rocks in the region.

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Mineralogic and climatic interpretations of the Late Miocene-Pliocene Red Clay Formation on the Chinese Loess Plateau

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The closest past analog to the contemporary global warming is the Pliocene. Its climate reconstruction has been focused on continuous sedimentary records and terrestrial eolian deposits. The late Miocene-Pliocene Red Clay Formation on the Chinese Loess Plateau is among the best archives of the Pliocene paleoclimate change. In this study, we examined three classic Red Clay profiles at Lingtai, Duanjiapo and Bajiazui on the Chinese Loess Plateau with X-ray diffraction, Fourier transform infrared spectroscopy, diffuse reflectance spectrophotometer and scanning electron microscopy. Compared to the overlying Pleistocene loess-paleosol sequences, the Red Clay profiles show the following different mineralogical features: (1) carbonates are composed of both calcite and protodolomite; (2) the protodolomite are rhombic euhedral crystals growing in soil voids and coexisting with secondary calcite and palygorskite; (3) smectite is one of the dominate clay minerals; (4) the hematite/goethite (Hm/Gt) ratio varies from 0.30 to 0.52, and is much higher than that of Quaternary loess and paleosol. The occurrences of protodolomite and palygorskite as well as abundant hematite and smectite in the Red Clay sequence may indicate that it was formed under a prevailing warm and dry climate condition, which is probably a response of the inner Asia continent to the Pacific permanent El Niño and global high temperature climate in the late Miocene to Pliocene.

Thermodynamic study for CO₂ storage in deep saline aquifers

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Storage of CO₂ in deep saline aquifers is one proposed option to limit the continuing buildup of greenhouse gases in the atmosphere. To reduce the capture costs, co-injection of CO₂ and H₂S is proposed. To predict the sequestration capacity and the fate of injected gases as well as for other geochemical applications, it is necessary to study the thermodynamic properties and phase equilibria for the CO₂ sequestration-related systems at temperatures up to 200 °C and pressures up to 600 bar.

A new thermodynamic model, on the basis of statistical associating fluid theory equation of state, is developed to represent the phase equilibria and thermodynamic properties for CO₂-H₂O-NaCl, H₂S-H₂O-NaCl, and CO₂-H₂S-H₂O-NaCl systems. The parameters of pure components are obtained from the fitting of their saturated vapour pressure and liquid density data, and the cross parameters are obtained from the fitting of the phase equilibrium data of H₂S (CO₂)-H₂O-NaCl system.[1-4] With the available parameters, the phase equilibria and thermodynamic properties for CO₂-H₂S-H₂O-NaCl are predicted. The prediction shows that the solubility of the H₂S-CO₂ mixture increases with increasing pressure, decreasing concentration of NaCl and decreasing temperature. The mixture of H₂S-CO₂ is more soluble than pure H₂S under certain conditions and also more soluble than pure CO₂.

This thermodynamic model will be further implemented into a dynamic model to investigate the process of gas diffusion and dissolution in brine and the process of mineral dissolution and precipitation with dissolved CO₂ and H₂S. It is expected that the coupling of the dynamic model with the thermodynamic model will provide reliable long-term predictions pertaining to geochemical carbon sequestration, such as sequestration capacity, CO₂ leakage, the mechanics of CO₂ trapping, and environmental impacts, etc.

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Detrital zircon provenance of late Ordovician-Silurian sandstones in the Lower Yangtze foreland basin of South China

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The Lower Yangtze foreland basin is situated northwest of the early Paleozoic (ca.460–400Ma) Wuyi orogenic belt in South China [1]. In this basin, the upper Neoproterozoic-Ordovician strata are composed of shelf carbonates, slope limestones as well as mudstones [2]. Significant changes of lithofacies, and depositional environment took place during latest Ordovician–Silurian, which were coincident with the timing of the Wuyi orogeny. In order to demonstrate the basin development was in response to the orogenic event, seven sandstone samples were collected from upper Ordovician and Silurian strata. U–Pb ages of 604 detrital zircon grains yield remarkable peaks at ca. 2500Ma, 1200–900Ma, 860–740Ma and 458–425 Ma. The early Paleozoic zircons (458–425 Ma) correspond to the granitic rocks within the Wuyi orogenic belt to south or southeast, suggesting exhumation of syn-orogenic rocks. Besides, the Precambrian zircons (ca. 2500Ma, 1200–900Ma, 860–740 Ma) are most likely recycled from pre-orogenic strata in the Wuyi orogenic belt due to their similarity in age distribution [2]. The predominant Neoproterozoic (860–740Ma) zircons indicate the Yangtze basement had been involved in the orogenic belt. The youngest zircons at the top of the succession yield a maximum depositional age of ca. 425 Ma.

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A major decline of C₄ plant in the source region of the North Pacific eolian dust (Asian interior) from 12 to 9 Ma

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Aeolian deposition in the central north Pacific has been well recognized to originate from arid Asian interior. However, works on terrestrial organic tracers therein are rare. In this work, higher plant leaf wax n-alkanes from ODP Site 1208 in the northwest Pacific since the middle Miocene were analyzed to explore the source region vegetation and climate changes. Both average chain length of wax n-alkanes and their accumulation rates showed a general increasing trend, consistent with the well recognized climatic drying trend of the Asian interior. The record of isotopic fractionation factor between plant and atmospheric CO₂ ($\epsilon_{\text{plant-CO}_2}$), calculated from $\delta^{13}\text{C}$ values of n-alkane and atmospheric CO₂, showed a prominent decrease from 12.4 to 9.3 Ma, and displayed a general pattern of higher values prior ~8 Ma and lower values post ~8 Ma. Although all values of $\epsilon_{\text{plant-CO}_2}$ (-18.5 to -16.8‰) were well within the range of C₃ plants, adjustment of isotopic discrimination of C₃ plants was ruled out as the main cause of the observed $\epsilon_{\text{plant-CO}_2}$ variations. Therefore, relative abundances of C₃ vs. C₄ plants were invoked to interpret the $\epsilon_{\text{plant-CO}_2}$ record, and higher C₄ contributions (13.8 ± 2.0%) were inferred due to slightly warmer climate in the source region prior to ~8 Ma. The suggested major C₄ decline from 12.4 to 9.3 Ma was concurrent with evidences supporting a prominent uplift of northern Tibetan plateau [1], demonstrating close relationships of Tibetan uplift, drying and cooling climates, and vegetation changes of the Asian interior.

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Geochemistry of the Xuanwei Group in Guizhou, Southwestern China

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Introduction

According to the regional geological information, the sedimentation of southwestern margin of the Yangtze plate was of platform type, its sedimentation in the Xuanwei Group was series of marine to land transformation association [1]. The Upper Permian Emeishan basalt group underlying contact with Xuanwei Group, is continental flood basalt [2], as an eruption of the Emeishan large igneous province magmatism [3]. Sedimentary environment is very useful to understand activities in the Emeishan large igneous province and geological event of great significance to the changed environmental process.

Methods and Results

Trace elements and strontium isotopes are measured of samples from the Xuanwei Group, west Guizhou, and we also collected data from publications from the Emeishan Group and its adjacent regions [1-3]. Based on analyses of petrochemistry and strontium isotopes of carbonaceous shale and sandy shale rocks, geochemical characteristics indicate that sedimentary environments show hydrothermal activity, accompanied with normal sedimentary participation. The fluctuations in Ce anomaly represent conversion process from oxidative environment and deoxidized environment. Strontium isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$)₀ manifesting that materials of the Xuanwei Group may be derived from Emeishan basalts mixed with marine carbonate from chemical weathering. It concludes that sedimentary sources were not only by Emeishan basalt weathering, but also causes of hot water sedimentary display.

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A 700-year record of accumulation rates at Dome A, Antarctica

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Dome A, located along the dividing line of East Antarctica, has the highest altitude in Antarctica. Preliminary evidence indicates that Dome A holds high potential for 'oldest ice' cores [1].

During the 21st Chinese Antarctic Research Expedition in 2004/2005 austral summer, a 109.91 m ice core (hereafter DA2005 ice core) was recovered at the site about 300 m away from the summit of Dome A. Chemical analysis of the DA2005 core has been used to construct continuous, detailed glaciochemical record. And time stratigraphic horizons from known volcanic eruptions were used for dating. Several clearly visible sulfate peaks in the top 35 m part of DA2005 were identified by comparison with common volcanic chronologies from Antarctica [2, 3]. These include the well-known volcanic events in the last millennium: Agung 1963, Krakatoa 1883, Tambora 1815 and an unknown eruption 1809, Unknown 1693, Kuwae 1453 and Unknown 1259. A mean accumulation rate was calculated according to the time stratigraphic horizons between two adjacent events and was assumed constant to date the intervening snow layers. Results show that the mean accumulation rates during different time periods are quite constant, ranging from 21.5 to 24.5 mmH₂O·yr⁻¹. And the resulting dates for other volcanic events during the period of 1259-1963 A.D. are in good agreement with those in previous Antarctic ice core volcanic records. The mean accumulation rate between Agung and 1259 A.D. is 23.2 mmH₂O·yr⁻¹, which is the same as the value between 1966 and 2004 A.D. measured from snow blocks collected at Dome A [4]. It seems that there is neither an indication of a change nor a trend in the accumulation rate apparent during the period of 1259-1963 A.D. which may indicate no drastic change in deposition has occurred at Dome A within this time period.

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Analysis of microbial molecular ecology techniques in constructed rapid infiltration system

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The microbial molecular ecology techniques, which were developed on the basis of molecular, were applied in studying the bacteria in Constructed Rapid Infiltration system (CRI). These techniques are very efficient in better describing the bacterial diversity, microbial community distribution and the relations between microbial group structure and nitrogen contamination through the analysis of microbial nucleic acid sequence fragment in CRI. The results further revealed the removal mechanism of contamination, which are essentially for the improvement of wastewater treatment in CRI.

In this study, a series of microbial molecular ecology techniques were applied in studying the bacteria in CRI. The microbial community distribution of bacteria was analyzed by PCR-DGGE qualitatively and a bacterial 16S rDNA gene clone library was constructed to analyze the bacterial diversity quantitatively. The anaerobic ammonium oxidation bacteria were proved to exist in CRI by phylogenetic analysis with a DNA sequence similarity of 97 %. The relations between microbial groups' structure and nitrogen contamination, and the removal mechanism of contamination were revealed.

Granularity and geochemistry of olivine in Jinchuan Ni-Cu-PGE magmatic sulfide deposit

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The Jinchuan Ni-Cu-PGE deposit is the third largest magmatic Ni deposit in the world, hosted by a small ultramafic intrusion in the Longshoushan terrane located in the south-western part of the North China Craton.

Granularity of olivine in the Jinchuan complex is from 1-8mm in diameter. Those olivine with 6-8mm distributes in ore-body 24, only contains disseminate sulfide; the olivine with 3-6mm still mainly lies in ore-body 24 contain partial net-texture sulfide; the olivine with 1-3mm in diameter distributes all mine, including most net-texture ore and no-sulfide rocks.

Our datum prove forsterite contents (mol. % Fo) of olivine in the Jinchuan rocks are in the range of 83.9-85.5% in pyroxene-bearing peridotite (no sulfide, olivine 1-2mm in diameter, at the surface of ore-body 2), 82-83.5% in dunite and lherzolite (mostly net-texture sulfide, olivine 1-3mm or 6-8mm in diameter, in ore-body 1, 24), and 78-81% in olivine pyroxenite (partial net-texture sulfide or no sulfide with tremolite, olivine 1-2mm in diameter, in ore-body 1, 2) (Fig.1). Little variation within one sample is observed for olivine.

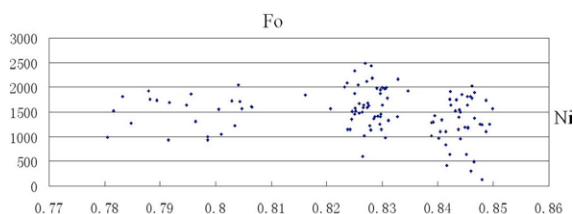


Figure 1: Compositional variations of different types of olivine from the Jinchuan rocks

So Granularity and forsterite contents of olivine have no accordant variation; Most net-texture sulfide ore holds forsterite contents from 82-83.5%, indicating the main ore-forming condition; 83.9-85% in pyroxene-bearing peridotite with no sulfide and stabilized Ni contents in olivine means olivine has partially crystallized before sulfur saturation as the decrease of temperature. Three type of forsterite contents means three types of rock-forming conditions, maybe three middle magma chambers.

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An Atomic Force Microscope study of the microstructure of 'barkinite' liptobiolith

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Using Atomic Force Microscope (AFM) to observe the surface of 'barkinite' and vitrinite in nanoscale, reveal the surface microstructures of 'barkinite' and vitrinite, that is, the netlike structure of vitrinite macromolecular clusters and the fiberlike, granular, and netlike structure of 'barkinite' macromolecular clusters. With increasing maturity, the structure of 'barkinite' macromolecular clusters are fiberlike - granular - irregular netlike - netlike in sequence (Fig.1), while the structure of vitrinite macromolecular clusters change from loose, irregular network to highly orient arranged, regular network. Quantitative analysis of the structure of macromolecular cluster and arrangement in maceral by using cross - section analysis tool of Atomic Force Microscope provide a new approach to study the structure evolution of maceral molecule and hydrocarbon generation mechanism.

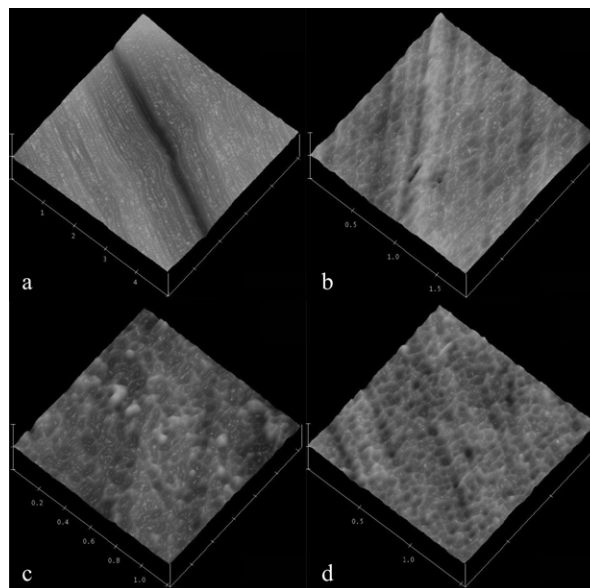


Figure 1: Microstructure evolution model of "barkinite" (a-gas coal, b-gas-fat coal, c-fat coking coal, d-anthracite)

Enhanced phosphorus regeneration in low oxygen marine settings: insights from modern and ancient sediments and implications for the future ocean

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Phosphorus (P) is a key nutrient for marine productivity and its availability plays a crucial role in the development of oxygen deficiency in marine systems. Most importantly, enhanced release of phosphate from seafloor sediments under low-oxygen conditions can drive a positive feedback loop between increased productivity, oxygen depletion and marine P availability. This feedback loop helps to sustain low oxygen conditions in restricted basins such as the Baltic Sea and may have contributed to the development of large-scale oceanic anoxia and massive burial of organic matter in the Earth's past. Here, we first summarize the field evidence for enhanced regeneration of P relative to organic carbon (C) from modern and ancient sediments. We then briefly review the responsible mechanisms, including enhanced regeneration of P from organic matter under low oxygen [1], and limited retention of P in inorganic minerals. We also present the results of an experimental investigation into the bacterial controls on P regeneration. Finally, we discuss the role that enhanced regeneration of P from sediments can play at the regional and global scale. We show that enhanced regeneration of P can account for the underestimation of phosphate concentrations in existing nutrient budgets of the Baltic Sea. Using biogeochemical ocean modeling, we show that oxygen depletion in the global ocean is also highly sensitive to the rate of enhanced regeneration of P. These results underline the need for improved quantitative and mechanistic understanding of the P cycle to better understand past changes in ocean oxygenation, and to predict those which may occur in the future.

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Ripening processes during crystallization of natrojarosite

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The crystallization behavior of jarosite type compounds $M\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ($M = \text{Na}^+, \text{H}_3\text{O}^+, \text{K}^+, \text{Ag}^+, \text{NH}_4^+$) has received increasing attention due to the formation of these minerals in acid mine water drainage environments during the oxidation of sulphide minerals. The fact that jarosites were identified on Mars gives these minerals an additional interest as indicators of water-limited chemical weathering on that planet. Although different jarosite-type compounds have been synthesised by precipitation at temperatures close to 100°C [1], the genesis of these minerals in environmental conditions needs to be studied in depth. In this work, natrojarosite was synthesized by mixing 60 ml of $\text{Fe}_3(\text{SO}_4)_2$ (1N) and 40 ml of NaOH (1N) parent solution at $25 \pm 0.1^\circ\text{C}$. Similar experiences were performed using 0.5N concentrations for both parent solutions (50:50 ratio). The experiments were carried out for specific reaction periods (1 day to 7 weeks) by keeping the solutions at constant agitation. The aging process of natrojarosite was followed by monitoring the precipitate crystallinity (X-ray diffraction), the aqueous solution composition (ICP-AES), and the pH.

Using 1N parent solutions, a low-crystallinity precipitate was obtained in the early stages of the experiments. However, as the reaction time passes by, the main XRD reflections (012, 021 and 113) of natrojarosite become more apparent and undergo a progressive decrease of widthness (FWHM) and an increase of intensity which indicate an increasing degree of crystallinity. In contrast, using 0.5N parent solutions the precipitate remained amorphous during the whole aging process. The pH values varied between 2.6 and 2.2, in all experiments. The aqueous solution exhibited a slight increase of both Fe and Na concentrations that is consistent with the development of the crystalline phase. Aqueous solution modellization (phreeqc code) evidenced higher saturation indices for hematite than for natrojarosite, which indicates that the formation of natrojarosite was governed by kinetic factors.

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Comparison of different evaluation schemes and optimization of instrumental parameters for chlorine isotope analysis of organic compounds using GC-qMS

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Compound specific chlorine isotope analysis is a valuable tool to detect and quantify biodegradation processes and abiotic transformation of chlorinated organic compounds in the subsurface. The new GC-qMS method avoids tedious off-line sample pretreatments and offers a quick and sensitive method for on-line determination of chlorine isotope ratios. In this study, the GC-qMS method for chlorine CSIA of chlorinated hydrocarbons was evaluated and validated. We compared the existing evaluation schemes to determine chlorine isotope ratios with newly proposed and/or modified ones. Besides, we tested the important instrumental settings such as split ratio, ionization energy and dwell times. Chlorinated ethenes were selected as model organic contaminants. Headspace sample of tetrachloroethene (PCE), trichloroethene (TCE) and cis-dichloroethene (cisDCE) at aqueous concentrations in the range of 20-500 $\mu\text{g/L}$ were analyzed using GC-qMS. The results showed good precisions (relative standard deviation: 0.4‰ - 2.1‰, n=5). We also found that the precision of the GC-qMS method depends on the applied evaluation schemes, instrumental parameters and target compounds. A systematic test and evaluation of these important factors enabled us to optimize the GC-qMS technique to determine the chlorine isotope ratios of chlorinated organic contaminants.

In situ Pb and U isotope analysis of single ostracod shells from Nam Co, Tibet

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We have developed a new LA-ICP-MS technique for combined *in situ* trace element, Pb and U isotope analysis of single ostracod shells. High spatial resolution is achieved by using spot sizes of 12 - 100 μm . We analyzed very small (ca. 0.5 mm) and thin (about 0.05 mm) shells from eight levels of a Holocene lake sediment core from Nam Co, Central Tibetan Plateau, deposited within the last 7700 a BP [1]. *In situ* measurements of (²³⁴U/²³⁸U), ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb yielded a precision (RSD) of about 2 % for U = 10 - 20 $\mu\text{g g}^{-1}$ and 0.2 % for Pb = 10 - 40 $\mu\text{g g}^{-1}$.

Our results show identical ratios for ostracods from the same core depth indicating that they reflect the composition of the lake water. (²³⁴U/²³⁸U) and ²⁰⁸Pb/²⁰⁶Pb show significant variability with age: Ostracods from the upper core section show uniform isotope ratios (1.42 ± 0.01 and 2.134 ± 0.003, respectively). The older samples show lower and more variable isotope ratios. These findings are in agreement with investigations of the sediments [1] and suggest that the isotope ratios of the ostracod shells reflect past climate variability: reduced precipitation and runoff, low lake level and maximum salinity since ca. 800 a BP, more humid conditions and a positive precipitation/evaporation balance between 5400 and 7200 a BP [1]. The lowest ratios ((²³⁴U/²³⁸U) = 1.13, ²⁰⁸Pb/²⁰⁶Pb = 2.112) are observed in a 6000 a old ostracod shell, where a high intensity of monsoonal precipitation, associated with elevated lake levels in Tibet, is recorded [1].

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On the duration and rates of fluid release from a dehydrating slab

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At subduction zones, seawater-altered oceanic lithosphere recycles back into the mantle, heats up during descent and releases fluids by devolatilization of hydrous minerals. Large-scale fluid flow resulting from this dehydration is implicit in recent models for the formation of arc magmas and appears to be linked to intraslab seismicity and non-volcanic tremors. However, the mechanisms as well as spatial and temporal scales of this fluid flow are only poorly known.

Exposures of veins (mineralized fractures) in oceanic lithosphere, metamorphosed at high pressures in subduction zones, provide direct evidence for fluid mobility within subducting slabs. We quantify the duration of dehydration-related fluid flow through subducting oceanic plates by investigating a high-pressure vein and its reaction selvage. Using a novel approach employing an array of radiogenic (Sr) and stable (Li, Ca) isotope data combined with Li-diffusion and reaction kinetic modelling, we demonstrate that large amounts of fluid can be transported along major conduits over km distances in a pulse-like manner through slabs over surprisingly short time periods of ~170 to as little as ~6 years.

This indicates that even though the overall slab dehydration is a continuous process, dehydrating slabs release their fluid by short-lived, channelized fluid-flow events, involving aseismic mobile hydraulic fractures that rapidly traverse the subducting slabs. Furthermore, the time for mineral reactions to reestablish thermodynamic equilibrium in rocks along the flow pathways is estimated to be at least three times shorter than that of the overall fluid-rock interaction. This indicates that local thermodynamic equilibrium is indeed a valid assumption for understanding fluid-mediated processes at high fluid-rock ratios and sluggish reaction kinetics are negligible.

Sedimentary basin acid sulfate weathering: Its recognition and palaeo-environmental implications in the Eucla Basin, South Australia

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'Acid Sulfate weathering' broadly describes soil and regolith materials that typically had an abundance of iron sulfides that have oxidised to sulphates. This redox process as well as other processes such as ferrolisis and microbiological functions are important producers of protons and therefore acidity within the regolith. Although previous studies have tended to focus on the soil management and sediment diagenesis and weathering geochemical implications, this study considers the significance of these processes from a sedimentary basin geochemical perspective. As such, further insights into basin-hinterland palaeo-environments and controls and the stratigraphic implications for the resulting regolith materials are gained. The study basin is the Eucla Basin, which is one of the world's largest on-shore Cainozoic basins, extending across Australia's central southern continental margin.

One of the major controls on palaeo- and contemporary acid-sulphate weathering within the Eucla Basin is the setting of regional groundwater systems within the Eocene marginal marine sediments in the basin. In geochemically reduced settings, typically below the watertable, the sediments contain an abundance of pyrite, whereas where these sediments have been oxidised, typically above the watertable, the pyrite has been oxidised and sulphates (which are now widely expressed as alunite found under many playa lake beds) and iron oxides (especially hematite but also goethite) are prevalent. These processes also have a profound influence on the mobility and reorganisation of Al and Si, largely derived from clay minerals such as smectite and kaolinite. This has resulted in the formation of authigenic clays (e.g. halloysite) and phreatic silicification (ie. groundwater silcretes) hosting abundant termite bioturbation preserved in the basin's geological record. Palaeo-watertables that may be linked to eustatic, climatic and tectonic variations are now being interpreted across large parts of this basin.

Redox transformations of iron in extremely low pH environments: Environmental and industrial implications

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Iron is a particularly important microbial resource in extremely acidic (pH <3) environments, where it serves not only as a micronutrient, but also as a major electron donor and/or acceptor. This is due primarily to the much greater stability of ferrous iron (even in oxygen-saturated liquors) and solubility of ferric iron in extremely acidic compared to neutral pH waters. Many different species of acidophilic prokaryotes are known to either catalyze the dissimilatory oxidation of ferrous iron or the dissimilatory reduction of ferric iron, while some can do both, depending on the prevailing environmental conditions.

Measurements of specific rates of iron oxidation by acidophilic bacteria have revealed significant differences between species. In general, specialized chemolithotrophs, such as *Leptospirillum* spp., exhibit significantly faster rates than more generalist mixotrophic and heterotrophic species, such as *Sulfobacillus* spp. and *Ferrimicrobium acidiphilum*. Measurement of specific rates of dissimilatory reduction of soluble ferric iron by *Acidiphilium cryptum* str. SJH have shown that these are often much greater than values recorded for neutrophiles. Rates of reductive dissolution of ferric minerals by acidophilic bacteria appear to depend on the relative acid-solubilities of the former. Acidophilic iron-reducing bacteria appear to use the often small amounts of ferric iron in solution, thereby causing the equilibrium between mineral-phase and solution-phase iron to move in the direction of the latter. Reductive dissolution (and concomitant release of associated metals and metalloids) of a wide range of ferric iron minerals, including jarosites, schwertmannite and goethite, has been demonstrated *in vitro*.

Recent developments that harness redox transformations of iron for industrial applications include remediation of mine waters using the recently characterised species *Ferrovum myxofaciens*, and the extraction of nickel from oxidized ores by causing the reductive dissolution of goethite. The latter represents a major development in 'biomining'.

Oxygen isotope exchange between H₂O and super critical CO₂: Lab experiments and field evidence

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Traditionally, the application of stable isotopes in Carbon Capture and Storage (CCS) projects has focused on $\delta^{13}\text{C}$ values of CO_2 to trace the migration of injected CO_2 in the subsurface. More recently the use of $\delta^{18}\text{O}$ values of both CO_2 and reservoir fluids has been proposed as a method for quantifying *in situ* CO_2 reservoir saturations due to oxygen isotope exchange between CO_2 and H_2O and subsequent changes in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values in the presence of high concentrations of CO_2 . To verify that oxygen isotope exchange between CO_2 and H_2O reaches equilibrium within days, and that $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values indeed change predictably due to the presence of CO_2 , a laboratory study was conducted to measure the isotope composition of H_2O , CO_2 , and dissolved inorganic carbon (DIC) at representative reservoir conditions (50°C and 19 MPa) and varying CO_2 pressures. Results obtained showed that $\delta^{18}\text{O}$ values of CO_2 were on average 36.4 ± 2.2 ‰ (1σ , $n = 15$) higher than those of water at all pressures up to and including reservoir pressure (19 MPa), in excellent agreement with the theoretically predicted isotope enrichment factor of 35.5 ‰ for the experimental temperature of 50°C. Since the fraction of oxygen sourced from CO_2 is related to the total volumetric saturations of CO_2 and water as a fraction of the total volume of the system, we conclude that changes in $\delta^{18}\text{O}$ values of reservoir fluids can be used to calculate reservoir saturations of CO_2 in CCS settings given that the $\delta^{18}\text{O}$ values of CO_2 and water are sufficiently distinct. This was confirmed by field data obtained from eight observation wells at the Pembina Cardium CO_2 Monitoring Pilot in Alberta (Canada). Arrival of injected CO_2 caused changes in the $\delta^{18}\text{O}$ values of reservoir fluids of up to 4 ‰, as well as increasing DIC, Ca and Fe concentrations in the reservoir fluids.

Updated dust-iron dissolution mechanism: Effects of organic acids, photolysis, and dust mineralogy

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Aeolian dust deposition to remote oceanic regions is a major atmospheric supply pathway of essential nutrients (e.g. iron (Fe) and phosphorus (P)) which have a controlling effect on marine primary productivity. The soluble/bioavailable fractions of Fe and P in mineral dust are minor at the source regions and increase during the transport. Nutrient mobilization from mineral dust is a complex process; in the atmosphere it is thought to be controlled by dust mineralogy, atmospheric chemical composition, and meteorological variables. Therefore, quantitative predictions for the formation of these important nutrients should be included in global-scale coupled biogeochemical cycle models for improved prediction of future climate.

Here, the global 3-D chemistry transport model GEOS-Chem with a state-of-the-art Fe- and P-dissolution scheme is used to generate comprehensive global datasets for nutrient concentrations and deposition (Fig. 1). The model improvements include source-specific dust-mineralogy, organic ligand-promoted Fe dissolution, the photolytic redox cycling of Fe (II)/Fe (III), and acid-based P dissolution. Preliminary results indicate that Fe bound in clay minerals and the presence of oxalate significantly increases soluble Fe production in mineral dust. Photolysis can further increase the amount of soluble Fe by converting Fe (III)-species into the more bioavailable ferrous Fe (Fe (II)) form. Model predicted diurnal variations in Fe (II)/Fe (III) are consistent with available data.

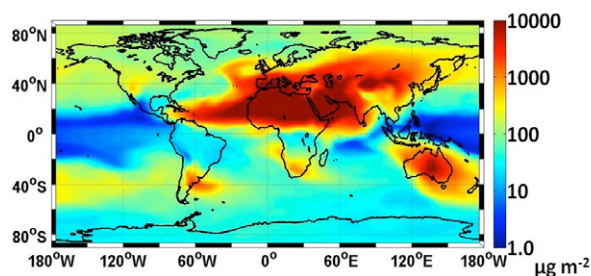


Figure 1: Model-predicted total column burden of soluble Fe ($\mu\text{g m}^{-2}$) between June-August 2009.

Adsorption of organic ligands on silicate mineral surfaces in the presence of CO₂ and water: Insight into olivine dissolution rates

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The dissolution of magnesium silicates releases magnesium cations (Mg^{2+}) into solution, which in the presence of dissolved carbon dioxide (CO_2) can, under certain conditions, precipitate as magnesium carbonates. This process results in the mineralization of CO_2 , a safe, long-term storage strategy to control rising CO_2 concentrations in the atmosphere. However, the kinetics for these processes are slow and the mechanisms are not fully understood. Previous work by this group and others has found the dissolution rates of silicates to be enhanced by the presence of organic acids in some cases, but reduced in other cases. This study seeks to understand the factors that determine whether an organic compound acts as an activator or an inhibitor. Organic ligands may adsorb to silicate surfaces as outer-sphere complexes, likely passivating active sites and reducing dissolution rates, or as inner-sphere complexes, drawing electron density away from the mineral surface, weakening near-surface bonds, and increasing dissolution rates. The nature of the adsorbed complexes depends on mineral surface charge and ligand charge, both of which are controlled by pH. X-ray photoelectron spectroscopy has been used to examine the organic carbon adsorbed on olivine and quartz surfaces after reaction with organic acids, water, and CO_2 . Initial results show additional carbon on the surfaces exposed to the organic-containing aqueous phase but none on surfaces exposed only to the supercritical CO_2 - H_2O phase. Mineral surfaces exposed to both the CO_2 and H_2O phases also showed increased superficial carbon.

Calibrating S isotope fractionation in sulfate reducing bacteria

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The sulfur isotopic composition of sedimentary sulfate and sulfide minerals throughout Earth history is a reflection of the activity of dissimilatory sulfate-reducing bacteria (SRB). The magnitude of the fractionation between sulfur compounds is interpreted as a biochemical consequence of changing environmental conditions. However, quantitatively understanding the isotopic variability within the geological record requires calibrating the physiological controls on dissimilatory sulfate reduction (e.g. sulfate concentrations, relevant electron donor, etc.). We have interrogated these controls with three complementary approaches.

First, through the incorporation of recent biochemical and crystal structure data, we have reexamined the reaction network involved in dissimilatory sulfate reduction. Our revised network adequately describes previous observations, and is experimentally testable.

Second, we measured the production of intermediates in pure cultures of *D. desulfuricans* grown on sulfate/sulfite and lactate/formate. In these experiments we observe the systematic production and consumption of sulfite and thiosulfate. We have tracked the isotopic consequences of each experiment, including the measurement of the site-specific isotopic composition of thiosulfate. These data reinforce our model predictions and provide valuable constraints on the fractionations associated with thiosulfate production and consumption.

Third, we performed community scale experiments in quasi-chemostat microbial reactors to better quantify changes in fractionation in response to sulfate concentrations. Whereas the pure culture work investigates the internal cycling, the reactor work assesses the first-order controls on sulfate uptake.

Through this broad combination of experimental and conceptual approaches, we provide unprecedented insight in the operation of the sulfate reduction pathway: information that can be used to better calibrate and inform our interpretation of sulfur isotopes in the sedimentary record.

Constraining magma-carbonate interaction at Vesuvius, Italy: Insights from stable isotopes and experimental petrology

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At Vesuvius volcano, Italy, abundant high temperature calc-silicate (skarn) xenoliths have been found in many eruptive deposits and, provide evidence for intense interaction between magma and carbonate crust. In order to understand magma-carbonate interaction and to quantify carbonate assimilation processes, we present a combined stable isotope study of natural samples and piston cylinder de-carbonation experiments.

The sample study shows that $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope values of igneous-, skarn- and carbonate rocks indicate that significant crustal contamination of Vesuvius magmas has taken place. Calc-silicate xenoliths define variable degrees of decarbonation and interaction processes between magma and crust, producing progressively more lava-like values [1].

In the experiments, we simulated the processes of carbonate assimilation under magmatic pressure and temperature conditions (0.5GPa and 1200°C) with Vesuvius magma composition and local crust as starting material. We have constructed a high-resolution time-sequence of magma-carbonate interaction in our experimental products with short but increasing dwell run-times (t_d), of 0, 60, 90 and 300 sec [2]. We observe a progressive carbonation of the host melt, and rapid liberation of large quantities of CO_2 coming from the breakdown of the enclosed carbonate. Variable degrees of carbonate assimilation and chemical mixing between carbonate and silicate melts are observed, with diffusion processes playing an important role at melt interfaces.

The combination of petrological evidences and experimental products allows insights into the processes and time-scales of magma-crust interaction and reinforces the hypotheses that carbonate assimilation is an ongoing and significant magmatic process at Mt. Vesuvius.

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[2] Deegan *et al.* (2010) *J. Petrol* **5**, 1027–1051.

Irregular retreat of tropical glaciers during the Holocene

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Causes and timing of tropical glacier fluctuations during the Holocene are poorly understood. We present a chronology for the past 11, 000 years of the Bolivian Telata glacier. We show that Telata glacier retreated irregularly. A rapid and strong melting from the maximum extent, at $10.8 \text{ ka} \pm 0.9$, to $8.5 \text{ ka} \pm 0.4$ ¹⁰Be years was followed by a slower retreat until the Little Ice Age (LIA) while a dramatic acceleration occurred over the 20th century. A glacier-climate model and additional climate constraints indicate that annual temperatures for this region were -3.3 ± 0.8 °C cooler at 11 ka BP and were -2.1 ± 0.8 °C below the present value until the end of the LIA. We suggest that low-frequency warming of the eastern tropical Pacific and increased atmospheric temperature in response to enhanced austral summer insolation were the main drivers for the long-term Holocene retreat of the glacier. Future temperature projections estimate a 4°-5°C warming in the tropical Andes by 2100, a warming close to our estimate for the whole Holocene.

Mineral composition of the metallurgical slag after steel production

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Introduction

Metallurgical slags are increasingly often used as material in production of aggregates, but there are also attempts made to recover metals from them. That is why it is important to carry out research on their mineral and chemical composition, which may deliver much valuable information during an economic exploitation of slags, e.g. connected with new phases forming in a metallurgical furnace, forms of metal occurrence in slag components and possibilities of their release from slag components and migration to the environment [1, 2].

Research results

The conducted mineralogical research of slags after steel production proves that among their phase components, apart from metal concentrations (including up to 98% Fe) and glaze, oxide and silicate phases are especially interesting because of their heterogeneous chemical composition.

Oxide phases are represented by iron oxides (magnetite, hematite, wustite), chromite, ilmenite and phases with compound chemical composition. We can recognize among them oxides Ca-Mg or Ca-Ti with elements of: Cr, Mn, Fe, Zn. A common component is also a solid solution of compounds: FeO, MgO, MnO occurring in variable quantity relations, with admixtures: V, Zn, Cr, Ti and Ca.

Among silicate phases there are distinguished, among others, pyroxenes from a series of augite, monticellites, wollastonite, dicalcium silicates (larnite). Their chemical composition is considerably diversified, and often differs from the chemical composition of the same phases forming in natural conditions. Silicate phases are also carriers of heavy metals, which may be included in their internal structures or form micro-inclusions. For instance, a considerable group consists of calcium silicates with admixtures of Ti, Cr, Mn, V, Mg and P, as well as calcium silicates and aluminosilicates Ca-Fe.

The scientific work is financed as a research project from the means allocated for science in the years 2010-2011.

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[2] Jonczy (2009) *Mineral Resources Management* **25**, 19–34.

A Precambrian manganous sea?

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Differences in the biogeochemical behavior of Fe and Mn can lead to their physical separation and a variation in the Fe:Mn ratio in sedimentary rocks. The mechanisms controlling the Fe:Mn ratios of Precambrian sedimentary rocks remain understudied. Using previously published data from the Mt. McRae shale deposit [1, 2] and the biogeochemical characteristics of Fe and Mn, we evaluate the potential controls on Fe and Mn co-deposition in this succession. We suggest that before the ‘whiff’ of oxygen, as recorded in the Mt. McRae shale, Fe and Mn were deposited together as carbonate minerals at a ratio reflecting their supply from hydrothermal fluids. During the ‘whiff’, iron likely precipitated and was sequestered in the sediments as sulfide minerals. This sulfide resulted from a global increase in the flux of sulfate to the oceans due to increased oxidative weathering on the continents [2]. We propose that this led to a global enhancement of Fe removal as Fe sulfides, preferentially enriching seawater in dissolved manganese relative to iron. In the Mt. McRae shale, we find evidence for this in the sediments deposited after the ‘whiff’, which exhibit a Mn enrichment relative to Fe with respect to both a hydrothermal source and continental weathering. These observations support the hypothesis of a transitional manganous ocean that punctuates intervals of ferruginous and euxinic ocean redox states [3]. We propose that enrichments of Mn relative to Fe in marine sediments deposited under anoxic conditions are a sensitive proxy for increased oxidative weathering.

[1] Anbar *et al.* (2007) *Science* **317**, 1903–1906. [2] Reinhard *et al.* (2009) *Science* **326**, 713–716. [3] Jones *et al.* (2011) *Biogeosci. Disc.* In press.

Ecological niches of Fe-oxidizing acidophiles in a coal mine discharge

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Low pH iron oxidation is a promising strategy for cost effective bioremediation of acidic mine drainage (AMD). To effectively utilize the iron-oxidizing potential of naturally-occurring microbiota in AMD discharges, knowledge of the diversity, iron-oxidizing efficiency, and natural distribution of acidophilic communities is required. Here we used full-cycle rRNA analyses to describe the composition of sediment communities at Red Eyes, an AMD site in Somerset County, PA, USA. Near anoxic emergences, the dominant microbial communities are green benthic *Euglena* biofilms and associated populations of *Gamma*- and *Betaproteobacteria*. As pH and Fe²⁺ concentrations decrease downstream, the dominant iron oxidizers shift first to (i) a close relative of *Gallionella spp.*, followed by (ii) *Ferrovum spp.*, and finally to (iii) *Acidithiobacillus ferrooxidans*. Archaea and *Leptospirillum spp.* are less than 2% of cells.

In previous research using laboratory reactors [1], we found that normalized iron-oxidation rates were 1.5–2x faster for the *Ferrovum*-dominated communities compared to the *Acidithiobacillus*-dominated communities. We have since extended our sampling and analyses to identify environmental variables that control the distribution of these and other iron-oxidizers at Red Eyes. Overall, turnover among communities is related to changes in pH and Eh. Results so far suggest that the transition between *Ferrovum*- and *Acidithiobacillus*-dominated communities depends on iron concentration rather than pH. Ongoing analyses will further define the ecological niches of these and other important AMD populations.

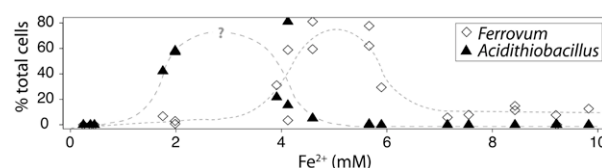


Figure 1. Fluorescence *in situ* hybridization cell counts of *Ferrovum* and *Acidithiobacillus* versus Fe²⁺ concentration.

[1] Brown *et al.* (2010) *Appl Environ Microbiol* **77**, 545–554.

Differential changes in Ni²⁺, Co²⁺ and Fe²⁺ coordination in silicate melt with pressure

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It is currently debated whether siderophile element abundances in the Earth's mantle reflect single-stage metal-silicate equilibration at high pressure at the base of an extensive magma ocean (homogeneous accretion), or the mixing of differentiated protoplanets each with a core formed at low pressures (heterogeneous accretion). This question has been addressed by parameterizing metal/silicate partition coefficients of siderophiles such as Ni, Co and Fe as a function of pressure, temperature and other variables, and extrapolating these parameterizations to determine P-T conditions that reconcile observed mantle abundances. Implicit in these parameterizations is that the partial molar volumes vary monotonically with pressure. XANES spectroscopy shows that the average coordination of Ni²⁺ in silicate glasses recovered from melts quenched at pressure, changes from tetrahedral to octahedral between 1 and 4 GPa, while that of Co²⁺ and Fe²⁺ remain unchanged. The effects of this transition are clearly mirrored in the distribution coefficients between iridium metal and silicate melt measured over the same range, showing that the quenched glasses reflect the liquid state at P and T. The partitioning can be modelled using different values of the partial molar volume of tetrahedral and octahedral NiO in the silicate melts. Changes in coordination environment of each siderophile in silicate melts will generally occur over different pressure intervals, preventing simple extrapolation of metal/silicate partitioning. The results enable an improved parameterization of the pressure dependence of Fe-Ni-Co partitioning, which excludes the simple single-stage magma-ocean hypothesis.

Martian magmatic volatiles recorded in olivine-bearing melt inclusions and matrix of shergottite Y-980459

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Martian basaltic meteorites [shergottites] contain a wealth of information about Mars. Of particular interest is the geochemical record contained in melt inclusions from the most primitive shergottite, Yamato 980459 (Y98). Using polished sections of Y98 mounted in indium to avoid volatile contamination from epoxy, our ion- and electron-microprobe study aims to constrain the volatile contents of primary Martian magmas generated by mantle melting. This record is also used to track the subsequent melt evolution of shergottite magmas. We report preliminary results for volatile abundances (H₂O, CO₂, S, Cl, F) in olivine-hosted melt inclusions (MI) and groundmass glasses (GG).

Unlike other shergottites, MIs in Y98 have remained glassy because of rapid cooling following eruption. Volatile concentrations of MI and GG in Y98 were analyzed by a Cameca ims-6f at DTM following the techniques of [1]. MIs contain distinctly higher contents of H₂O (~200 ppm) and CO₂ (600-1600 ppm) than GGs (<100 ppm H₂O and <20 ppm CO₂). In contrast, the MIs contain lower amounts of F (~15 ppm) and S (~900 ppm) than those in the GGs (~25 ppm F and 2200-3000 ppm S). Cl contents are almost constant among the MIs and GGs (~50 ppm). The CO₂ solubility in basaltic magmas suggests that the MIs were trapped at a depth of ~3 kbar. The pre-erupted magmatic water contents recorded in the Y98 MIs are ~2 orders of magnitudes lower than those proposed by the wet shergottite magma hypothesis (e.g. 1.8 % [2]), although the absolute water abundances in the MIs may have been changed by post-entrapment modifications. By using Na as an indicator of the degree of crystal fractionation (mainly olivine + pyroxene), the degree of degassing between pre-erupted (MI) and erupted (GG) Y98 melts are estimated as follows: CO₂ (~100 %) > H₂O (>80%) > Cl (50-70 %) > F (~0 %) ≈ S (~0 %, probably saturated with sulfide). Likewise, we estimate that the bulk Y98 liquid contained <30 ppm H₂O, 200-500 ppm CO₂, ~20 ppm Cl, ~5 ppm F, and ~300 ppm S.

[1] Hauri *et al.* (2002) *Chem. Geol.* **183**, 99-114. [2] McSween *et al.* (2001) *Nature* **409**, 487-490.

Incongruent dissolution of volcanic riverine particulate material in seawater: Consequences for global element cycling

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The world's rivers transport material from the land to the oceans in dissolved form and as particulate matter. Although particulate fluxes dominate over dissolved fluxes for the majority of elements relatively little attention has been paid to the role of riverine particulate material, both in the fluxes of elements to the oceans and moderating global climate [1]. The degree to which riverine particulate matter plays a role in the compositional evolution of seawater depends on its dissolution rate after arrival in the ocean. Volcanic islands supply the most easily weathered material to the oceans and are an important component of the global suspended flux. However, the apparent dearth of original volcanic minerals in oceanic drill cores suggests that the dissolution of riverine particulate material in seawater may be an important component of land-to-ocean element fluxes.

This study measured directly the initial element release rates of riverine particulate material in seawater through a series of closed-system batch reactor experiments. Large changes to the concentrations and isotopic ratios of elements are observed in seawater when mixed with riverine particulates. Elements such as Si, Ca, Mn and Ba show marked increases in seawater concentrations, indicative of particulate dissolution. Other elements such as Li become rapidly depleted in seawater, suggesting element exchange reactions or the formation of secondary phases. Sr and Nd display comparatively little change in seawater concentrations, but have large changes in isotopic ratios. Taken together, these results demonstrate a significant role of seawater weathering of riverine particulate material to the fluxes of elements to the oceans and have important consequences for the use of isotopes as tracers of global processes.

[1] Gislason *et al.* (2006) *Geology* **34**, 49–52.

Fluid and temperature conditions in an oceanic detachment fault footwall: Insights from late-stage mineral veins (ODP Leg 304/305)

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The Atlantis Massif is an oceanic core complex located at the Mid-Atlantic Ridge at ca. 30°N. During IODP Leg 304/305 Hole U1309D the footwall of the detachment fault, which is related to exhumation of the Massif, was drilled. It consists mainly of gabbros and troctolites, with minor amounts of basaltic and ultramafic rocks. The 1416 m long drilled section is fractured and shows a retrograde overprint recorded by granulite- to zeolite-facies mineral assemblages. Late-stage mineral veins (consisting of anhydrite, calcite, prehnite or zeolite) formed from sub-seafloor fluid-rock interactions. These veins were examined to further our understanding of the fluid regime and temperature conditions in detachment fault systems.

Abundant syn- to postkinematic calcite has low concentrations of incompatible elements (e.g. U, Sr, Li) as well as flat chondrite-normalized REE+Y pattern with a positive Eu anomaly. This indicates that the calcite precipitating fluids are similar to basalt-hosted high-T vents and indicate no affinity to the nearby serpentinization-derived Lost City vent field. The deep origin of the fluids is highlighted by low ⁸⁷Sr/⁸⁶Sr (0.704 to 0.708), mantle-like $\delta^{7}\text{Li}_{\text{LSVEC}}$ (+0.8 to +9.4‰) and $\delta^{13}\text{C}_{\text{PDB}}$ (-6 to -2‰). From $\delta^{18}\text{O}$ values, minimum calcite precipitation temperatures of 150–220°C are derived.

Anhydrite and anhydrite + zeolite veins have ⁸⁷Sr/⁸⁶Sr values consistent with anhydrite formation from down-flowing seawater which had leached only minor amounts of Sr from the basement. The REE pattern of anhydrite veins indicate that admixed hydrothermal fluids at depth played a minor role.

Silicate minerals (prehnite, quartz, plagioclase) predominate veins in the deepest section of Hole 1309D and indicate precipitation temperatures ranging from 270 to 145°C (estimated from $\delta^{18}\text{O}$ values). They are comparatively unradiogenic in ⁸⁷Sr/⁸⁶Sr (0.7033–0.7046) and demonstrate (in contrast to anhydrite) enhanced intensity of reactions between infiltration seawater and basement with increasing depth.

Surface properties and complexation on titanium dioxide nanoparticles

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There is an increasing amount of synthetic nanoparticles in the environment. Due to their small size, they have properties that result in higher reactivity compared with larger particles and bulk materials. Interactions that occur at the surface of nanoparticles are important for understanding and predicting nanoparticle fate and behavior, as well as characterizing the potential risks for the environment and human health.

Surfactant-free TiO₂ nanoparticles were synthesized and characterized according to [1]. Temperature during synthesis reaction, dialysis and storage was found to strongly influence the particle size and crystal structure. Potentiometric titrations were used to determine the surface charge of the particles at varying pH and ionic strength.

In order to mimic the interactions of nanoparticles with natural organic matter (NOM), surface complexation on TiO₂ was studied using model organic substances possessing carboxyl and hydroxyl groups. Results show that the adsorption of 2, 3-dihydroxybenzoic acid (2, 3-DHBA) was influenced by pH, and the amount adsorbed varied greatly with initial TiO₂ particle size. The size dependent surface complexation is investigated further in order to obtain a mechanistic understanding of the processes that occur at the molecular level when TiO₂ nanoparticles interact with NOM.

Further, the stability of TiO₂ nanoparticle dispersions in presence and absence of well-characterized macromolecules (sodium alginate, humic acid, and fulvic acid) was studied in different electrolyte environments and at varying pH. The aggregation behavior was investigated by monitoring the changes in particle size using dynamic light scattering.

[1] Abbas *et al.* (2011) *Colloids Surf. A, Physicochem. Eng. Aspects*, doi, 10.1016/j.colsurfa.2011.03.064

Stable carbon isotope chemostratigraphy and implications for global carbon cycling, Cretaceous Western interior basin

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The Late Cretaceous provides a critical analog for the anthropogenic greenhouse world. Strata of 100 Ma±20 myr record one of the warmest times in Earth history and are characterized by high-resolution time control, global correlation of deposits from deep ocean to epicontinental seas, and a series of global scale perturbations of the land-ocean-climate system. These perturbations include major changes in carbon cycling, surface temperatures, glacial ice volumes, sea level, and marine redox conditions over geologically short intervals (10's – 100's of kyr, similar to durations predicted for an anthropogenic greenhouse forced by combustion of all fossil fuel reserves). Recent findings from the Cenomanian-Turonian Ocean Anoxic Event 2 (OAE2), one of the largest Cretaceous events, have implicated active volcanism from emplacement of the Caribbean large igneous province as a trigger. One approach to testing this hypothesis involves carbon isotopes, since a volcanically triggered OAE should leave a characteristic signal. This study reports a new Cenomanian to Campanian carbon isotope record for the central Western Interior basin linked to a carbon isotope mass balance model. Major perturbations in the isotope record, such as Mid-Cenomanian Event and OAE2, are correlated to other carbon isotope records and analyzed with a series of model experiments. The new δ¹³C record contributes to Late Cretaceous chemostratigraphy and allows testing of the volcanic initiation hypothesis, as well as the role of regional variations in organic matter burial.

Speciation of trivalent metal ions at the silica/water interface studied by second harmonic generation

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The nonlinear optical technique of second harmonic generation (SHG) is used to study the interactions of Al (III), Y (III), La (III), and Gd (III) with the fused silica/water interface. Specifically, the Eisenthal $\chi^{(3)}$ technique [1] is employed in order to quantify several thermodynamic binding parameters of these ions as a function of background electrolyte concentration. Using this highly surface specific technique, we are able to quantify binding constants, adsorption free energies, absolute number densities, and interfacial charge densities in real-time and without the use of labels. We also examine the relationship between the measured adsorption free energies and the electric double layer interfacial potential at each electrolyte concentration to elucidate the charge state and possible binding pathways for each ion at the fused silica surface.

Our results show that the binding of each trivalent ion is fully reversible under the experimental conditions employed in this study. Adsorption isotherms are measured under dynamic flow conditions and fit using the Triple Layer model. We employ an analysis that takes advantage of the additive adsorption free energy expression in which the observed free energy is modeled as a sum of the electrostatic free energy and the intrinsic chemical free energy [2]. From this analysis, we find that the Al (III) ion binds to the fused silica surface as a fully hydrated trivalent species in a bidentate geometry. In contrast, the Y (III), La (III), and Gd (III) ions are each shown to adsorb to the silica surface in a reduced valence state. Despite identical oxidation state, the extent and mode of binding varies between each ion. These SHG studies provide valuable data that can be used to predict the transport these metal ions are throughout the environment.

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Hydrate destabilization and methane release events during last glacial episode in Bay of Bengal

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We report here for first time episodic methane expulsion events in the Krishna-Godavari basin, Bay of Bengal during the marine isotope stage 4 (MIS-4) and at the transition of MIS-4 and MIS-5. We have observed sharp negative carbon isotope excursions in the isotope profiles of planktonic (*G. ruber*) and benthic (*Uvigerina sp.*) foraminifera in a core MD161-8, recovered on board *Marion Dufresne* as part of our gas hydrate exploration program in 2007. Depleted carbon isotope excursions in both benthic (B₁, B₂ and B₃) and planktonic (P₄, P₅ and P₆) foraminifera suggest that the methane expulsion events not only altered the carbon stable isotopic composition of the bicarbonate pool near the sediment waters interface, but also that of the shallow water column. A significant fraction of methane gets oxidized to HCO₃⁻ via anaerobic methane oxidation (AMO) at or below the sediment water interface. Depletion in carbon stable isotope ratios of the dissolved inorganic carbonate (DIC) pool depends on the carbon stable isotope ratios of methane advecting from deeper layers. Reported $\delta^{13}\text{C}_{\text{CH}_4}$ values (-75 to -85 ‰ VPDB) and C1/C2+C3 ratios (1110 to 3354) suggest presence of biogenic hydrocarbon gases within the methanogenic zone at the site MD161-8. Carbon stable isotope ratios of infaunal benthic foraminifera like *Uvigerina sp.* may get significantly influenced by incorporation of isotopically depleted carbon as HCO₃⁻ in the calcitic shell during growth and considered as a potential proxy for paleo-methane seepage. On the other hand, the depleted carbon isotope excursions recorded for the corresponding planktonic foraminifera, *G. ruber*, suggests that a part of the expelled methane reached the upper mixed layer (0-25m) where aerobic methanotrophy resulted in the depletion of carbon stable isotope ratios of the DIC reservoir.

We attribute the methane emission events to destabilization of the base of gas hydrate stability zone (BGHSZ) due to shale tectonics induced focused fluid flow. Fluid released from the over-pressured mud, possibly played important role in creating fractures as well as advection of the gases in K-G basin.

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Clumped isotope measurements to reveal diagenetic histories

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Clumped isotope geochemistry is a growing field, and more particularly the 'carbonate clumped isotope paleothermometer' is becoming more widely applied. Isotopologues are molecules that are identical except for their isotopic composition. Clumped isotopes are isotopologues where two or more heavy isotopes are clumped together; the effects of clumping are enhanced with decreasing temperatures, the zero point energy of the system being lowered. However, calibrating clumped isotopes is still a novel and challenging field of research, and more importantly measuring isotopologues requires skills and high sensitivity mass spectrometry.

So far, clumped isotopes have been used mainly in paleoclimate research. Here, we intend to calibrate the carbonate clumped isotope paleothermometer for diagenetic material. Carbonates are reactive minerals that can easily be modified during burial and exhumation. Post-depositional diagenetic processes such as dissolution and re-precipitation of new minerals are common and result in modified mineralogical and petro-physical characteristics of the initial carbonate rock. Temperature at which those transformations occur is a fundamental parameter in diagenesis: given a known geothermal gradient and burial history, the temperature of precipitation of carbonate cements can be translated into depth and timing of the event, assuming a thermal equilibrium between the fluids and the rock. Because it is thermodynamically based, the clumped isotope paleothermometer is independent of the isotopic composition of the diagenetic fluid and therefore can be applied with greater confidence.

We are currently implementing the technique at Imperial College London, both in a manual and in an automatic manner. Our aim is to improve the technique in order to be able to measure smaller sample sizes of diagenetic material (such as cement and crack infills) and to lower the associated error down to $\pm 1^\circ\text{C}$. We are therefore running a wide range of calibrations, on calcite and dolomite, and from different synthetically precipitated carbonate materials.

Ultimately, we aim to constrain the depositional and diagenetic environments of selected outcrops in Oman in the context of a wider study on Carbon Capture and Storage.

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A ~ 3.63 Ga major impact recorded by the Bunburra Rockhole anomalous basaltic achondrite

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The Bunburra Rockhole (BR) meteorite is an anomalous basaltic achondrite recovered in Western Australia [1]. BR mineralogy, petrology [1] and mineral composition [2] resemble classical brecciated basaltic eucrites, generally associated with asteroid 4 Vesta. However, BR oxygen isotopic composition is distinct from the general HED fractionation line, suggesting that BR, along with 3 other anomalous eucrites, belongs to a distinct differentiated parent asteroid. Previous chronology studies indicate a reset of the ²⁶Al-²⁶Mg system and a ~ 4.1 Ga ²⁰⁷Pb-²⁰⁶Pb whole-rock re-equilibration age for BR [2].

The ⁴⁰Ar/³⁹Ar chronometer has typical low closure temperature of few hundred °C and has the potential to record heating events such as large collisions between asteroids. We have analyzed 4 groundmass (fine-grained) and 5 breccia (medium- to coarse-grained) single-grain aliquots of BR using the ⁴⁰Ar/³⁹Ar laser step-heating technique. All samples yielded well-defined plateau ages. 7 grains yielded a weighted mean age of 3634 ± 18 Ma (P=0.53) suggesting that BR recorded a major impact event on its parent body at this time. 2 breccia grains suggest a secondary minor heating event at 3538 ± 24 Ma (P=0.54).

Generally, eucrites ⁴⁰Ar/³⁹Ar analyses yield complex age spectra with ambiguous apparent ages between 3.4 and 4.1 Ga [3]. Here, a unique well-defined age at 3.63 ± 0.02 Ga based on several flat age spectra indicate that BR had a simpler history than eucrites from Vesta 4 and may suggest that BR belongs to a different parent asteroid.

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Cu isotopes suggest Cu reduction during acquisition in higher plants

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Evidences from recent studies suggest that studying the natural isotope fractionation of metals in plants offers great potential to elucidate acquisition and translocation mechanisms. We conducted controlled hydroponic studies with lettuce, tomato, rice and durum wheat and tested the effect of copper (Cu) speciation and iron (Fe) supply in the nutrient solution. Next to Cu isotopes, we studied the zinc (Zn) isotopes since Zn is not sensitive to redox processes and a model of Zn isotopic fractionation in plants has been proposed [1].

Isotope fractionation patterns between nutrient solution, roots and shoots differ for Cu and Zn. Roots are enriched in ⁶³Cu (light isotope) but slightly enriched in Zn heavier isotopes compared to the nutrient solutions, suggesting that different processes occur for Cu and Zn at the root-solution interface. Different physical, chemical and biological processes can contribute to the isotopic fractionation during acquisition of Cu and Zn by plants. Abiotic processes, mainly complexation in the nutrient solution or adsorption onto root binding site, are expected to fractionate similarly for Cu and Zn. On the contrary, plant behaviour differs for Cu and Zn, as seen with the concentrations and isotopic ratios data.

The enrichment in light isotopes for Cu is associated with significant reduction of Cu at the root-solution interface, suggesting that this biogeochemical mechanism is predominant for the acquisition of this metal into plants. This is similar to mechanism of Fe uptake for strategy I plant species [2].

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How are oceanic δ¹⁸O changes imprinted in ice core records?

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The deuterium and oxygen 18 composition of a precipitation and thus its deuterium-excess, $d = \delta D - 8 \delta^{18}O$, depends, amongst other parameters, on the isotopic composition of surface waters in the oceanic source regions. As a result, the glacial-interglacial $\delta^{18}O$ change of surface oceanic waters is imprinted in the ice core d-excess record with, in Central Antarctica, a 3 to 4 ‰ d-excess increase directly attributable to the oceanic source. In the same line, changes in oceanic $\delta^{18}O$, globally averaged in this case, influence the $\delta^{18}O$ composition of atmospheric oxygen directly through oceanic productivity and indirectly over the continent. Obviously there are many other processes, most of them however relatively well identified, which govern the $\delta^{18}O$ oceanic record derived from foraminifera, on the one hand, and the d-excess and the air $\delta^{18}O$ measured respectively in polar ice and entrapped air bubbles, on the other. In this context, we will compare the amplitude and time sequence of these three isotopic signals from one deglaciation to the next, thanks to the d-excess and air $\delta^{18}O$ records now available on nine terminations from the EPICA Dome C ice core.

Nucleation and growth mechanisms and kinetics of environmentally important oxides and carbonates

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Nucleation and growth of hydrous oxide or carbonate nanoparticles can significantly influence the fate and transport of organic and heavy metal contaminants in the environment. Their particles' formation and transport can alter the porosity and permeability of geo-media. Therefore, more accurate quantitative and qualitative information about mineral nucleation and growth is required.

In this work, we used a time-resolved simultaneous small angle x-ray scattering (SAXS)/grazing incidence (GISAXS) setup for real-time monitoring of water-mineral interfacial reactions. To observe the size, shape, distribution, and phase of hydrous iron oxide and calcium carbonate nanoparticles on quartz and mica surfaces as well as in solutions, we also used complementary techniques, such as atomic force microscopy, high resolution transmission electron microscopy, high resolution X-ray diffraction, and grazing incidence wide angle x-ray scattering. The solutions included different ionic strengths of sodium nitrate, arsenate, aluminum, and polyaspartate. The mineral nucleation and growth modes were monitored as a function of exposure time. We delineated the quantitative contributions between homogenous and heterogeneous mechanisms at varied environmental conditions. Hydrous iron oxide nanoparticles formed preferentially along steps rather than terraces, while amorphous calcium carbonate did not show any clear preference. Under aqueous conditions, newly formed nanoparticles did not exhibit any facets. The presence of arsenate and aluminum ions significantly influenced the sizes and crystallinities of hydrous iron oxide nanoparticles and altered their nucleation and growth kinetics. This study provides more accurate depiction of nucleation and growth of environmentally important minerals in solution as well as at active interfaces. Our findings have implications not only for hydrous oxide- or carbonate-containing biogeochemical systems, but also for environmental remediation (heavy metal removal and nuclear waste deposition site remediation) and geoengineering applications (geologic CO₂ sequestration).

Effects of organic ligands on supercritical CO₂-induced phlogopite dissolution and secondary mineral formation

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To evaluate the long-term and short-term risks associated with geologic CO₂ sequestration (GCS), we need to understand both the reactions at supercritical CO₂ (scCO₂)-saline water-rock interfaces and the environmental factors affecting these interactions.[1, 2] This research investigated the effects of four organic ligands (oxalate, malonate, acetate, and propionate) on the dissolution and surface morphological changes of phlogopite [KMg_{2.87}Si_{3.07}Al_{1.23}O₁₀(F, OH)₂] under GCS conditions (in particular, 95°C and 102 atm). Phlogopite was chosen as a model clay mineral in potential GCS sites.

After CO₂ injection, the dissolution of CO₂ causes a pH decrease in saline water, which increases phlogopite dissolution, but this effect can be minimized by the buffering capacity of organic ligands. However, in this study, for ligands forming a strong complexation with surface metals, phlogopite dissolution rates (especially for Al) are increased by ligand-promoted dissolution, even though the pH increases. The experimentally observed dissolution rates of phlogopite were in the order: oxalate > malonate > acetate ≈ propionate. Based on results from ion-exchange chromatography, oxalate and malonate were stable in our reaction system; however, acetate and propionate concentrations continuously decreased due to the solvent extraction of acetic acid and propionic acid by scCO₂ at 95°C and 102 atm. After 159 h, all of the acetate and propionate had disappeared from the aqueous solutions.

Interestingly, in the presence of oxalate, nanoscale precipitation of amorphous silica and fibrous illite was observed only three hours after CO₂ injection. At this early reaction time, illite fibers formed a honeycomb structure on phlogopite basal surfaces, but at a later reaction time these structures detached from the surface and triggered the formation of dissolution channels. In addition, kaolinite, boehmite, diaspore, and gibbsite were also identified. These results provide new information for understanding reactions at scCO₂-saline water-rock interfaces in deep saline aquifers.

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Laser-induced breakdown detection (LIBD) of uranium and silica colloids

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Introduction

Laser-induced breakdown detection (LIBD) is a well established technique using plasma formation in the high irradiance of a focused laser beam for measuring small size of colloidal particles in an aquatic environment. Over the last decades, several different LIBD systems which adopt different detection schemes by using a piezoelectric transducer, a charge-coupled device camera, and an optical probe beam were developed. These LIBD systems enable to detect extremely low concentration of nanoparticles. Thus, the LIBD technology can be applied in various fields such as, *in situ* observation of colloid mediated transport of pollutants and measurement of solubility of radio-active elements.

Although LIBD methods allow one to determine a particle size in principle, until now, particle sizing capabilities in most LIBD experiments were inspected only for polystyrene particles of a well-defined size as a reference material. Therefore, it should be certified that these LIBD methods are whether suitable or not to determine the particle size for different materials.

Discussion of Results

In the present work, particle sizing capability using LIBD has been investigated for three different materials: uranium, polystyrene, and silica nanoparticles. It was observed that spatial distribution of breakdown events generated by laser pulse of 532 nm wavelength along the laser beam propagation axis was directly correlated with particle size for uranium and polystyrene, while there was no correlation between the spatial distribution of breakdown events and particle size for silica. The reason for these phenomena is understood based on the ionization potential (IP) of each material. IPs of these materials are about 6.17, 7.8, and 11.7 eV for UO_2 , polystyrene, and SiO_2 , respectively. When a focused laser pulse of 532 nm wavelength is used to generate laser-induced plasma, simultaneous three or four photon absorption is required to induce multiphoton ionization (MPI) of uranium and polystyrene. However, at least five photon absorption is required to induce MPI of silica. The result suggests that determination of particle size of silica particles with the aid of calibration curve obtained from the polystyrene reference particles may give incorrect values.

Seismic anisotropy produced by serpentine in the mantle wedge

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Trench-parallel seismic anisotropy has been observed in many subduction zones in the upper mantle. In this study, crystal-preferred orientation (CPO) and seismic anisotropy of natural serpentine from Val Malenco in northern Italy and Punta Bettolina in western Italy were studied. It is found that [010] axes are aligned subnormal to the foliation but [010] axes of serpentine are aligned subparallel to the lineation which is significantly different from that produced in a recent high-pressure experiment. I show that the CPOs of serpentine found in this study can be used to explain trench-parallel seismic anisotropy in the mantle wedge, not only for serpentine deformed at high angles greater than 45° from the surface but also for serpentine deformed at low angles such as in horizontal shear, demonstrating that the CPO of serpentine has much broader implications for interpreting the seismic anisotropy than previously thought. It is also found that seismic anisotropy caused by the CPO of serpentine depends on the degree of serpentinization and flow geometry. Current data suggest that trench-parallel seismic anisotropy in the forearc mantle wedge in subduction zones can be attributed to the CPO of serpentine.

Wadi as collectors of drinking water in South Mongolia

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Current drinking water resources of south Mongolia do not yield suitable quality and quantity to often. Solution of the drinking water deficit issue can partially solve the large wadi evaluation, such as drinking water collectors. We constructed the first evaluation of wadi water capacity for Khan Bogd complex, which is one of the largest known intrusions of peralkaline granite (*ca.* 1500 km²). Watersheds and stream network and profiles carefully identified in the field were verified by comparison of supervised classifications of Landsat TM images. The possible sources yield almost 5.0×10⁶ m³ and average annual recharge rate for the Khan Bogd wadi aquifers is estimated at 1.892×10⁶ m³. The only risk of the aquifer contamination presents stock, but comparing the chemical composition of the water from wells used for animals feeding and samples of groundwater, we didn't observe any important contamination (ammonium up to 10 mg/l). Present study is the first attempt to describe and evaluate the potential wadi Khan Bogd as a source of drinking water in the Mongolia. Implication for use of this new water source accessible for drinking water in whole arid region of South Mongolia is clear.

Distinguishing mantle derived contributions at a continental arc volcano: Tatar-San Pedro

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Subduction recycling plays a key role in the distribution of elements between the mantle and crust. One of the important challenges in the study of arc magma genesis is identifying contributions from the subducted slab and mantle, and distinguishing them from crustal contamination at relatively thick crust continental arc volcanoes [1, 2]. The Quaternary Tatar-San Pedro complex (TSPC) of the Southern Volcanic Zone (SVZ) is a large, compositionally diverse frontal arc volcanic complex. High-density sampling has yielded one of the most complete eruptive chrono-stratigraphies (spanning over 930 kyr) of any arc volcano [3, 4, 5]. This provides us with a unique opportunity to elucidate magma source heterogeneity and the effects of recycled slab, mantle, and crustal input at a continental arc volcano.

This study augments an extensive XRF geochemical dataset with new isotope and ICP trace element analyses. Although most TSPC lavas appear impacted by crustal input, we distinguish three distinct mantle-derived magma types: (1) one derived from 'depleted mantle' fluxed by slab-derived hydrous fluids (high Sr/Nd, Zr/Nb and low ⁸⁷Sr/⁸⁶Sr), (2) one from 'enriched mantle' (high incompatible elements, HFSE, and ⁸⁷Sr/⁸⁶Sr), and (3) another that appears prevalent to the SVZ mantle wedge (subduction modified) with generally intermediate but still distinct chemistry (broadly similar to parental magmas at other SVZ volcanoes). Extensive MASH processing is precluded by the absence of significant garnet fractionation in the endmembers and by eruption of diverse parental magmas over short time intervals.

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