Siderite in Archaean banded iron formations - A sensor for CO₂ partial pressures of ancient atmospheres?

F.M. GÄB1*, C. BALLHAUS1 and J. SIEMENS2

1Steinmann Institut, Universität Bonn, Germany
2Institute for Crop Science and Resource Conservation-Soil Science, Universität Bonn, Germany

It has been around for some time that siderite in Archaean BIFs can serve as a CO₂ sensor for Archaean atmospheric compositions [1], according to

\[ \text{Fe}^2+ (\text{aq}) + 3\text{H}_2\text{O} + \text{CO}_2 (\text{atm}) = \text{FeCO}_3 \text{ (siderite)} + 2\text{H}_3\text{O}^+ (\text{aq}) \]

This equilibrium is seemingly shifted to the right as the CO₂ partial pressure (pCO₂) of the atmosphere rises, triggering the precipitation of marine carbonates including siderite if there is sufficient Fe²⁺ (aq) dissolved in seawater. In reality, rising pCO₂ causes the H₂O activity increase (ocean acidification), lowering the CO₃²⁻/HCO₃⁻ activity ratio in water until carbonate minerals become unstable. Hence, the above equilibrium is metastable and unviable to describe natural atmosphere-seawater interactions, contrary to assertions by Ohmoto et al. [1]. We are equilibrating natural and artificial seawater at 25°C with oxidized N₂-O₂-CO₂ and reduced N₂-CH₄-H₂-CO₂ atmospheres with variable pCO₂ ranging from 10⁻³ to 1 atm. Up to a pCO₂ of ~ 0.05 atm, the carbonate alkalinity of seawater is independent of pCO₂ as predicted by thermodynamics, however, when pCO₂ increases above 0.07 atm (pH < 6.5) carbonate alkalinitites gradually decline and carbonate minerals become unstable. Carbonate minerals find ideal conditions when the pCO₂ of the atmosphere is at its minimum and the CO₃²⁻/HCO₃⁻ activity ratio in seawater at its maximum (i.e. high weathering rates, low atmospheric pCO₂).

When the pCO₂ < 2*10⁻⁴ atm (< 200 ppm CO₂ in the gas phase), natural seawater at 25°C spontaneously precipitates aragonite in the form of micro-ooides. The precipitation of siderite in Fe²⁺-doped seawater equilibrated with a reduced atmosphere is impossible, so long as the water contains the current marine Ca²⁺ concentration. In an artificial, NaCl-NaHCO₃-FeCl₂-bearing, Ca²⁺-free seawater proxy (100 ppm Fe²⁺, carbonate alkalinity 4000 µmol kg⁻¹), falling pCO₂ causes the precipitation of an amorphous blue-green phase that we tentatively identify as ferrous-ferric carbonate hydrate.

Precipitation of that phases lowers the carbonate alkalinity by around 40 percent. That phase may qualify as precursor to siderite and could be an important primary precipitate from Archaean seawater. We conclude that siderite is not likely to be a primary precipitate from Archaean seawater. We further conclude that potential precursor phases to siderite (i.e. amorphous Fe-carbonate-hydrates) are most stable at maximum CO₃²⁻/HCO₃⁻ activity ratios in the water, hence are favoured at atmospheric compositions poor in CO₂.


Growth rate effect on oxygen isotope fractionation between calcite and fluid: In situ data

R.I. GABITOV *, A.K. SCHMITT1, E.B. WATSON2, K.D. MCKEEGAN1 AND T.M. HARRISON 1

1University of California, Los Angeles, CA, 90095, USA
2Rensselaer Polytechnic Institute, Troy, NY, 12180, USA

The oxygen-18 content of carbonates (expressed as δ¹⁸O) is widely used in paleoclimatology, yet it is clear from comparison between experimental and natural carbonates that isotopic equilibrium is not always achieved. This observation underscores the importance of exploring possible effects of growth rate on isotopic fractionation, which is the focus of this study.

In situ Secondary Ion Mass Spectrometry (SIMS) analyses of δ¹⁸O were performed on single crystals of experimentally grown calcite at an external reproducibility of 0.25 ‰ (1σ). Growth rate (V) variations within crystals grown isothermally (at 15, 20, 22, and 25°C) were monitored by sequentially spiking calcite-precipitating fluids with rare earth element (REE) dopants. The REE were analyzed with SIMS at spots matching those where δ¹⁸O was determined. REE patterns reveal concentric domains of calcite growth. The growth rate of calcite generally decreases with time - i.e., crystal rims advanced at slower rates than cores. The compositions of δ¹⁸O in bulk calcites and experimental fluids were measured by Fisons Optima and Finnigan MAT 251 mass spectrometers, respectively. The average of SIMS δ¹⁸O values agrees with bulk δ¹⁸O determined by conventional mass spectrometry within analytical uncertainty. The fractionation factor ε¹⁸O decreases by 0.8±0.08 ‰ with increasing V (0.12– 16 µm/day) at 25°C. If the core is included at an estimated V>30 µm/day, a total range of 1.7 ‰ is observed at 25°C. A maximum difference of 3 ‰ was observed between the rim and core of the calcite crystal grown at 15°C.

Our results provide the first in situ evidence that ¹⁸O may be depleted in the near-surface region of calcite relative to the bulk crystal lattice, consistent with the surface entrapment model [1]. As predicted, this effect increases with decreasing temperature. Therefore, knowledge of crystal growth rates needs to be accounted for when using δ¹⁸O in natural carbonates as a proxy for sea-water temperature.

Post-entrapment changes to H2O and CO2 in olivine-hosted melt inclusions

GLENN GAETANI1*, JULIE O’LEARY1,2 AND NOBUMICHI SHIMIZU1
1Geology & Geophysics, Woods Hole Oceanographic Institution, Woods Hole MA 02543 USA
(*correspondence: ggaetani@whoi.edu)
2ExxonMobil Production Company, Houston TX 77067

Olivine-hosted melt inclusions are an important source of data on magmatic volatiles. The strength of the olivine protects inclusions from decompression and degassing during ascent and eruption, preserving pre-eruptive volatiles. However, inferring mantle volatiles requires that melt inclusions remain closed systems from the time of entrapment. We used a combination of experiments and modelling to investigate the potential for post-entrapment modification of H2O and CO2. Our results demonstrate that proton diffusion re-equilibrates H2O in a matter of hours, but that a significant flux of C through the host olivine is unlikely. However, H2O changes can affect CO2 through the formation of vapor bubbles within the inclusion. The combination of diffusive re-equilibration and vapor bubble formation significantly affect degassing paths and entrapment pressures inferred from the volatile content of melt inclusions.

Effects of diffusive re-equilibration were assessed using hydration and dehydration experiments performed on natural inclusion-bearing olivines. All run products were analyzed for major elements by electron microprobe and for H2O and D/H ratio by SIMS. The oxidation state of Fe was determined by μ-XANES. Our results demonstrate that proton diffusion is extremely efficient at modifying the concentration of H2O in melt inclusions. These changes do not affect the fugacity of oxygen within the inclusion, which is controlled by the creation or destruction of metal vacancies that diffuse through the olivine at rates comparable to protons.

Initially vapor-saturated inclusions are driven toward undersaturation by the loss of H2O, so that the concentration of CO2 is not significantly effected. This produces melt inclusions with variable CO2 at constant H2O, resulting in an apparent open-system degassing path. Conversely, the addition of H2O to melt inclusions, as during magma mixing, drives inclusions toward vapor oversaturation, leading to the production of CO2-rich vapor bubbles. Therefore, the addition of H2O will cause melt inclusions to evolve along an isobaric CO2 degassing path, leading to significant changes in both H2O and CO2.

Causes and consequences of Zn, Fe and S isotope fractionation in a large hydrothermal system:
The Navan orebody, Ireland

D. GAGNEVIN1, A.J. BOYCE2, C.D. BARRIE2, J.F. MENUGE1* AND R.J. BLAKEMAN3
1School of Geological Sciences, University College Dublin, Belfield, Dublin 4, Ireland
(*correspondence: j.f.menuge@ucd.ie)
2SUERC, East Kilbride, Glasgow G75 0QF, Scotland
3Boliden Tara Mines Limited, Navan, County Meath, Ireland

This study investigates the extent, causes and consequences of Zn and Fe isotope fractionation within the world-class Irish-type Navan Zn-Pb orebody, Ireland. Layered sphalerite (ZnS) has been targeted for isotopic analyses. Using samples of growth-layered sphalerite, as well as bulk Zn ore concentrates and potential source rocks, we are able to examine processes of fractionation ranging from millimeter to kilometer scales.

Large variations in δ66Zn (of 0.55‰), δ56Fe (of 2‰) and δ34S (of 28‰) have been measured in microdrilled sphalerite. Significantly, the range of δ66Zn (0.33‰) and δ34S (0.95‰) across 3 mm of sphalerite colloform growth banding represents a substantial fraction of the range exhibited by common terrestrial rocks. Moreover, δ66Zn and δ56Fe display a well-defined positive correlation and both also correlate with δ34S. S isotope compositions have previously been proven to monitor the extent of mixing between shallow, metal-poor, surface brines and deep, metal-rich, hydrothermal fluids in Irish-type deposits. The observed relationships represent the interplay between kinetic Zn and Fe isotope fractionation during sphalerite precipitation, and mixing of S between hydrothermal fluids and bacteriogenic brines.

Concentrate data clearly show that relatively high δ56Fe and δ66Zn dominate the overall system, and that lower δ56Fe and δ66Zn found associated with hydrothermal sulphide are a minor component of the overall deposit signature. Basement rock δ66Zn data confirm that the basement is isotopically not homogenous, nor homogenised in the hydrothermal system.

Our data suggest that incoming pulses of metal-rich hydrothermal fluid triggered sulphide mineralisation, and that rapid precipitation of sphalerite from hydrothermal fluids will strongly fractionate Zn and Fe isotopes at very short time and length scales, thereby limiting the use of Fe and Zn isotopes as exploration tools. However, Zn and Fe isotopes in sulphides appear to be powerful tools to assess and decipher the physical and chemical processes responsible for the genesis of ore bodies.
Minor elements in layered sphalerite record fluid origin in the giant Navan Zn-Pb orebody, Ireland

D. GAGNEVIN1*, J.F. MENUGE1, A. KRONZ2, C.D. BARRIE1 AND A.J. BOYCE3

1UCD School of Geological Sciences, University College Dublin, Belfield, Dublin 4, Ireland
(*correspondence: damien.gagnevin@ucd.ie)
2Georg-August-Universität Göttingen, Germany
3S.U.E.R.C, East Kilbride, Glasgow, Scotland

This study aims to test whether the chemistry of sphalerite in the world-class, Irish-type, Navan ore deposit may help to decipher the nature and origin of the ore-forming fluids. Detailed electron microprobe traverses were carried out across colloform and other growth-layered sphalerite, on samples that were previously analysed for Zn, Fe and S isotopes (Gagnevin et al., Goldschmidt 2011). In particular, the S isotope data enabled us to distinguish between samples that precipitated from hydrothermal, metal-bearing fluids or from cooler, bacteriogenic, sulphide-bearing fluids.

On the hand sample scale, Cd and Fe discriminate between the two fluid sources (Fig. 1); Cd, Sb, and to a lesser extent Cu, are enriched in sphalerite precipitated from hydrothermal fluids ($\delta^{34}S > 0$), while Fe and As are enriched in sphalerite precipitated from bacteriogenic fluids ($\delta^{34}S < 0$), suggesting that sphalerite chemistry is a good guide to fluid origin.

Figure 1: Cd vs Fe concentrations of layered sphalerite investigated in this study.

Frequent large (up to order of magnitude) elemental variations between successive sphalerite layers, whether colloform or not, indicate repeated influxes of hydrothermal fluids, with probable control also from kinetic effects and substitution mechanisms. Moreover, we show that sphalerite texture is sometimes, but usually not, correlated with sphalerite chemical composition.

Calcium isotopes during coral biomineralization

A.C. GAGNON1,2*, D.J. DEPAOLO1, J.F. ADKINS3 AND J.J. DE YOREO2

1Earth Sciences Division, Lawrence Berkeley National Lab, USA (*correspondence: acgagnon@lbl.gov)
2Molecular Foundry, Lawrence Berkeley National Lab, USA
3Geological and Planetary Sciences, Caltech, USA

A mechanistic understanding of biomineralization promises to separate biological and environmental signals in skeletal carbonates, improving the interpretation of paleoproxies. Towards this goal, we measure calcium isotope ratios of micromilled samples from modern scleractinian deep-sea coral, testing two questions in coral biomineralization. Is amorphous calcium carbonate (ACC) an important precursor during skeletal nucleation? Can reservoir effects (Rayleigh models) explain the biologically controlled variability of non-traditional stable isotopes.

Centers of calcification (COCs) are morphologically and compositionally distinct regions of the coral skeleton associated with nucleation. To test if an ACC precursor phase can explain the geochemistry of COCs, we compare the calcium isotope ratios of COCs to synthetic ACC. The $\delta^{44}Ca$ of COCs are similar to the surrounding skeleton and to inorganically precipitated aragonite, but are fractionated significantly more than inorganic ACC ($\Delta^{44}Ca_{\text{ACC:solution}} = -1.0 \pm 0.1 \%$ while $\Delta^{44}Ca_{\text{ACC:solution}} = -0.2 \%$). If ACC is involved in skeletal nucleation, then the distinct calcium isotope signature of this phase is lost during subsequent phase transformation. As calcium is the major cation in aragonite, this presumably means the minor and trace element composition of an ACC phase would be altered as well, and suggests that ACC is unlikely to explain the compositional anomalies associated with COCs in coral.

Even when grown under constant environmental conditions, metal/calcium ratios in deep-sea coral vary by more than 5%. This variability can be explained by skeletal precipitation from closed batches of seawater or a more general steady-state reservoir effect where seawater transport to the site of calcification balances precipitation. Both models make similar predictions regarding calcium isotopes, higher skeletal Sr/Ca ratios should correlate with lighter $\delta^{44}Ca$. We observe this predicted trend in preliminary results from micromilled samples, suggesting that in addition to metal/calcium ratios, reservoir effect models of coral biomineralization may also explain the variability of some isotope systems. Analysis of coral from a range of conditions will test if we can recover biomineralization corrected records of seawater isotope ratios and environmental conditions.
**Volcanic gases and redox biogeochemistry at the Archean-Proterozoic transition**

**FABRICE GAILLARD¹, BRUNO SCAILLET¹ AND NICHOLAS T. ARNDT²**

¹Institut des Sciences de la Terre d’Orléans, CNRS-INSU/Université d’Orléans, 45071, Orléans, France
²ISTerre, Université Joseph Fourier de Grenoble, CNRS, 38400, Saint Martin d’Hères, France.

A major crust-forming event at 2.7 Ga preceded a major change in the chemistry of surface waters on ancient Earth. Formation of a permanently oxygenated atmosphere at 2.45 Ga dramatically affected redox processes in the exosphere, as recorded in the ancient sulphur biogeochemical cycle. The emergence of oxygenic cyanobacteria and changes in composition of volcanic gases are possible triggers of the rise of atmospheric oxygen, but the sequence of these events and the evidence for such changes are debated. In particular, robust geochemical data indicates that the oxidation state of volcanic rocks and their source regions has remained constant since 3.5 Ga.

Using thermodynamic calculations simulating gas-melt equilibria during magma ascent, we show that change in the average pressure of volcanic degassing due to a global decrease in sea level accompanying the growth of the continental crust provides a simple yet robust explanation: Archean volcanic degassing was mostly submarine, occurring under water pressures of 10-100 bar and producing gases with H₂S/SO₂ >1, with low sulphur content. In contrast emergence of the continents in the late Archean led to widespread subaerial volcanism that yielded gases much richer in S and dominated by SO₂. The transition from H₂S dominated gases at elevated pressure of degassing to SO₂ dominated ones at atmospheric pressure is redox-compensated by a strong H₂ enrichment in the gas.

Archean and early Proterozoic sulphur biogeochemical cycles can be explained by a change in composition of volcanic gases that is unrelated to a change in magmatic source processes but most likely caused by geodynamic and eustatic modifications. The resulting changes in volcanic gas compositions must have impacted on the oxygenation of the atmosphere.

**The subduction weathering factory**

**J. GAILLARDET*, P. LOUVAT*, C. DESSERT AND E. LAJEUNESSE**

Institut de Physique du Globe de Paris, UMR 7451, Sorbonne Paris Cité. 75238 PARIS Cedex 05

About 30% of the global consumption of atmospheric CO₂ is due to the weathering reactions involving volcanic rocks. Therefore, volcanic settings are essential to consider both in terms of fluxes and mechanisms of chemical weathering. However few studies have focused on the weathering of volcanic arc islands although it is a key geodynamical setting, for example for the production of continental crust. Most of the degassing of deep CO₂ occurs in subduction zones and subduction volcanism is particularly rich in volatiles, such as sulfuric or chlorhydric acids that are major suppliers of acidity to the earth’s surface.

The synthesis of available data on river chemistry in volcanic arc setting and new data from our group on the rivers of Lesser Antilles show that the chemical denudation rates are amongst the highest on earth. They range from 10 t/km²/yr to 700 t/km²/yr in the most active regions.

Two dominant mechanisms appear to play the major roles in the subduction zone factory. The first is hydrothermal activity, the second is water runoff; the former being linked to the latter though the water cycle. Hydrothermal activity produces high temperatures and additional acidity in the form of sulfuric, chlorhydric and carbonic acids. Runoff values are generally associated to high precipitation regimes, due to the orographic effect. The orographic effect is temperature-dependent based on the Clausius-Clapeyron relationship.

Due to these two main mechanisms, subduction weathering factory transforms the rocks into sediments at a very high rate and is responsible for high CO₂ consumption rates. Our study suggests that chemical denudation is a significant fraction of the total erosion rate of volcanic arcs and that total erosion rates are in the order of the long-term magmatic eruptive rates.
On the peculiarities of Australian and Venezuelan pink diamonds: 
Influence of the geologic settings 

E. GAILLOU1,2, J.E. POST1 AND J.E. BUTLER3

1Department of Mineral Sciences, Smithsonian Institution, 
Washington, DC 20560, USA.
2Department of Terrestrial Magnetism, Carnegie Institute, 
Washington DC 20015, USA.
3Chemistry Division, Naval Research Laboratory, Washington 
DC 20375, USA.

Pink diamonds have a heterogeneous color that typically is restricted to lamellae formed by plastic deformation oriented along {111}. Pink diamonds from Argyle in Australia and from Santa Elena in Venezuela show distinct visual and spectroscopic features compared to diamonds from other localities. Their pink color is prominent and has a banded pattern, sometimes wavy, interlaced with smaller bands of colorless areas. The birefringence indicates that the plastic deformation is located mostly inside the colorless areas for Argyle and Santa Elena diamonds, and inside the pink areas for other diamonds. Cathodoluminescence (CL) images show that plastic deformation features cut across the growth patterns of the diamonds. They quench partially the CL in colorless areas, while the pink areas retain growth sectors, as delineated in CL images by H3 and N3 centers. For other pink diamonds, the colored lamellae contain H3 and 405.5 nm centers. It is possible that for Argyle and Santa Elena diamonds, a pre-existing pink color was partially quenched during a later episode of plastic deformation. Conversely, diamonds from other localities apparently acquired their pink color from a later stage of plastic deformation. The geological settings of diamonds from Argyle in Australia and Santa Elena in Venezuela are similar, forming underneath Proterozoic cratons (and not the typical Archean cratons), that experienced high thermal events in their early histories.

Potential for widespread microbial liberation of structurally-coordinated iron from common clay minerals in marine sediments 

ROBERT R. GAINES1, JOHNSON TRANG1, 
SAMUEL SCOTT1, E.J. CRANE1, MARIA PROKOPENKO2 
AND WILLIAM M. BERELSON2

1Pomona College, Claremont, CA, 91711, 
(robert.gaines@pomona.edu; 
jt012007@mymail.pomona.edu; sws1@hi.is; 
ej.crane@pomona.edu)
2University of Southern California, Los Angeles, CA, 90089, 
(prokopen@usc.edu; berelson@usc.edu)

Clay minerals are the most abundant materials found at the surface of earth and they are the primary constituents of marine sediments. Iron, a limiting nutrient in many marine settings, is a common constituent of clay minerals. Recent in vitro experimental evidence has shown that lab cultures of Fe-reducing bacteria are able to utilize structurally-bound Fe from the crystal lattice of nontronite, an uncommon and particularly Fe-rich smectite (>12wt.%). Reduction of structurally-coordinated Fe results in liberation of Fe(II) to solution, where it is available for other biotic processes, and the transformation of smectite to illite. However, it has remained unclear: 1. whether or Fe-reducers are able to access structurally coordinated Fe found in low wt.% in common clay minerals; 2. if naturally occurring populations of Fe-reducers are able to reduce structurally coordinated Fe as some lab strains are; and 3. if this process is significant in the marine Fe-cycle. In order to address these questions, we combined in vitro experiments using a suite of clay minerals with iron contents ranging from low (0.8 wt.%) to high (13.9 wt.%) with high-resolution analyses of sediment cores from the Santa Monica Basin, a location noted for a high benthic flux of Fe(II) from the sediments. Experimental evidence clearly indicates that, under in vitro conditions, Fe(III) bound in common clay minerals is available for reduction by the lab strain Shewanella oneidensis MR-1 as well as by naturally-occurring consortia of Fe-reducers cultured from the San Pedro and Santa Monica Basins. Analyses of sediment cores suggest that structural Fe bound in illite-smectite mixed layer clays (~3.0wt.%) of the Santa Monica Basin is bioavailable. Depth of smectite-illite conversion (<20cm) suggests that Fe may be liberated on the timescale of decades to ~200 years, contributing to the flux of Fe(II) from the sediments. Our findings suggest that common clay minerals may represent a large and previously unrecognized pool of bioavailable Fe in the world ocean that contributes significantly to biogeochemical cycling of Fe and C.
Experimental studies on CO₂ sequestration in basaltic rocks with a plug flow reactor

I. GALECZKA*, D. WOLFF-BOENISCH, AND S. R. GISLASON

Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavik, Iceland (*img3@hi.is)

Mineral trapping in silicate rocks is considered the most stable strategy of CO₂ storage. Conceptual model of CO₂ mineral fixation in Iceland assumes that acidic carbonated waters injected into basaltic rocks will initially cause rock dissolution and release of divalent cations such as Ca²⁺, Mg²⁺ and Fe²⁺. As reactions progress, these elements will combine with CO₃²⁻ and precipitate as carbonates due to increasing pH [1]. A large scale experiment with a plug flow reactor imitating chemical and physical conditions within the basaltic rocks after CO₂ injection, gives an opportunity to study the rate of basaltic rock dissolution and solid replacement reactions under controlled CO₂ conditions. The experimental set-up makes it possible to follow changes in pH, Eh and chemical composition of the fluid on different levels along the flow path within the column. Characterization and quantification of secondary minerals (carbonates and clays) enables determination of molar volume and porosity changes with time. Data obtained from experiment will be used in reactive transport models to elucidate the advance of reaction fronts, forecast porosity changes followed by estimation of upper limit CO₂ injected into a given geological formation.

Experimental set-up consists of 7 titanium compartments assembled into a 2.5 m long pipe (5.4 cm OD x 5 cm ID), corresponding to a volume of ~ 5 dm³. The column is filled with basaltic glass grains, of known chemical composition and surface characteristic (45-100 µm size fraction). CO₂ saturated water will be pumped under 75 bar pressure through the column. This contribution will present first preliminary results from this column experiment.


Stable Sr isotopes in seawater

S.J.G. GALER*, A. KRABBENHÖFT, W. ABOUCHAMI, G. BORGÄSSER AND H. FELDMANN

Max-Planck-Institut für Chemie, Postfach 3060, 55020 Mainz, Germany (*steve.galer@mpic.de)

Early work on dissolved Sr in GEOSECS ocean profiles from the Atlantic and Pacific showed Sr/salt variations with depth, providing evidence for depletion of dissolved Sr in surface waters [1]. This depletion was attributed to uptake of Sr from surface waters by acantharians, whose skeleton is made of celestite (SrSO₄), which subsequently dissolves at depth, thus exerting a control on strontium cycling in the water column [2].

We explore the potential of stable Sr isotopes as a tracer of such nutrient-like behaviour in seawater. We have analysed surface seawater samples and a depth profile collected in the Southern Ocean during GEOTRACES cruise ANT-XXIV-3 along the Greenwich Meridian, as well as the NASS-4 standard and a deep-water North Atlantic sample. The Sr isotope data were obtained using a ⁴⁰Sr-⁴⁰Sr double spike by TIMS at MPI. Measured δ¹⁸⁶⁶⁸/⁸⁶Sr obtained on the same samples are effectively homogeneous with an average value of 0.83 ± 0.04‰ (total range) relative to SRM 915a.

The ⁸⁸Sr/⁸⁶Sr of both surface water and depth profile samples gave a consistent value of 0.709176±8 (range) relative to 0.710250±7 (2SD) for SRM 987. The ⁸⁸Sr/⁸⁶Sr ratios, expressed as δ¹⁸⁸⁶⁶⁸Sr, show little variation in the deep waters, averaging 0.35±0.02‰. In contrast, surface waters show subtle variations along the transect (0.33±0.02‰) just within error of that in deep waters. The Southern Ocean compositions tend to be isotopically slightly lighter, overall, than those of the Atlantic further north (0.36±0.02‰), and as measured for IAPSO seawater [3, 4].

These preliminary data suggest that constancy of δ¹⁸⁸⁶⁶⁸Sr in seawater cannot be assumed a priori. Any variations thus far appear to lie on the edge of the analytical precision. Nevertheless, mapping the ocean δ¹⁸⁸⁶⁶⁸Sr distribution appears to be an important task, and may help elucidate the internal biological cycling of strontium in the water column.


Mineralogical Magazine www.minersoc.org
Continuum model for diffusive transport in the electrical double layer and clay interlamellae

J.M. GALINDEZ1*, C.I. STEEFEL1 AND U. MAEDER2
1Lawrence Berkeley National Laboratory, One Cyclotron
Road, Berkeley, CA 94720, USA
(*correspondence: JMGalindez@lbl.gov)
2Universität Bern, Switzerland (urs.maeder@geo.unibe.ch)

A continuum model for diffusive transport in the electrical double layer and the interlamellar space in clays is presented. The model makes use of a Donnan equilibrium assumption to calculate explicitly the composition of the diffuse double layer given an arbitrary bulk solution composition. In this approach, rather than solving the Poisson-Boltzmann equation explicitly, an average electrostatic potential corresponding to the double layer is computed. In the model, the double layer balances the charge of the mineral surface, which may be fixed charge (as in the case of ion exchange) or dynamically computed charge using a surface complexation model. In the case of clay interlamellae, the charge of the clay is fixed and the ions occupying the space are treated as part of a double layer that may or may not be overlapping. Diffusive transport is handled with the Nernst-Planck equation, with accounting for the local immobile charge of the mineral surface. The approach allows for modeling of anion exclusion in clay-rich materials, as well as ion exchange within clay interlamellae and edges.

Based on the same theoretical foundations as the single-type porosity model developed by Birgersson and Karnland [1], this continuum model provides identical predictions as long as the entire pore space is assumed to be occupied by the electrical double diffuse layer as, e.g., in highly compacted clays. These predictions were in turn validated by comparison with diffusion experiments conducted by Van Loon et al. [2].

The present work also explores the limitations of a discrete two-type porosity model in reproducing the actual continuous distribution of ion concentrations over the pore space as obtained with analytical expressions for very simple cases involving a pore space confined between two parallel electrically charged walls and saturated with a binary salt.


Geochemistry of nickel isotopes in ferromanganese crusts

L.GALL1*, H.M. WILLIAMS2, C. SIEBERT1 AND A.N. HALLIDAY1
1Department of Earth Sciences, University of Oxford, Oxford, OX1 3AN, UK
(*correspondence: louiseg@earth.ox.ac.uk)
2Department of Earth Sciences, University of Durham, Durham, DH1 3LE, UK

The stable isotope behavior of nickel (Ni) has not been studied as intensively as those of other transition metals (e.g. Fe and Mo), even though Ni is ubiquitous in many geological environments and a bioessential trace metal, for example in the production of methane by methanogens [1]. In this study we have measured the mass-dependent isotope composition of Ni (δ60Ni, relative to Ni SRM 986) in a variety of terrestrial samples by MC-ICPMS [2].

Our results demonstrate that there are significant variations in δ60Ni in nature (-0.5 – 2.5‰). The Ni isotopic composition of 8 samples of igneous and mantle rocks is effectively homogeneous, with only small variations (<0.2‰) between different rock types. In contrast we find that ferromanganese crusts are much heavier. We analysed surface scrapings from 20 hydrogenetic crusts, including samples from all major ocean basins. The average δ60Ni value for these crusts is +1.65‰ with a variation of ±0.4‰. There is no systematic variation with geographical position, water depth, or Ni concentration. However, given the residence time of Ni in the oceans (10,000 yr [3]), Ni isotope variations in ferromanganese crusts might reflect extreme local effects, such as differences in isotopic composition of source materials, input from hydrothermal vents, and fractionation during removal of Ni from seawater and adsorption. Further studies are needed to identify the specific processes. However, our data clearly demonstrate mass dependent fractionation of Ni isotopes in the marine environment.


Mineralogical Magazine www.minersoc.org
The Prestige oil spill after a decade: Evaluation of remediation strategies and the role of bioremediation.

J.R. GALLEGO1*, A.I. PELÁEZ1, J. SÁNCHEZ1, M.J. GCIÁ- MTNEZ2, J.E. ORTIZ2, T. TORRES2 AND J.F. LLAMAS2

2ETSMinas, Universidad Politécnica de Madrid. C/Ríos Rosas, 21-28003 Madrid, Spain.

In 2002, the Atlantic and Cantabrian shorelines of Spain were affected by the Prestige heavy fuel oil spill. Initially the fuel was physically removed in rocky areas by means of hot pressurized water washing and similar procedures, whereas in sandy beaches other machinery was used. However, bioremediation was also considered given that the destructive effects of the hot pressurized water on the biota, the difficulties to collect oily waste, and other questions related with the grain-size of the sediments affected and the strong fuel adhesion in the shore rocks [1, 2, 3].

Our research carried out several studies all along the coasts in which natural attenuation, biostimulation and bioaugmentation techniques were tested in pilot and full-scale experiments for remediating oil-coated sands, gravels, pebbles, cobbles and boulders. Microbiological control and normalization by means of non-degradable chemical biomarkers were made to monitor these procedures. To improve bioremediation yields, novel in situ fresh-water irrigation and on-site techniques were developed, following similar strategies than those habitually used in soil remediation. The results obtained underscored the utility of these innovative designs to be used as an alternative to the limited effectiveness of the application of oleophilic fertilizers, clearly limited by the recalcitrance and by the reduced bioavailability of resin and asphaltene fractions. As a conclusion, long-term strategies for the bioremediation of other spillages with similar characteristics are suggested.


Evidence of Fe-oxide clusters in obsidians

L. GALOISY, G. CALAS AND N. MENGUY

Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), UPMC; Université Paris 7; CNRS; 4, Place Jussieu, 75252 Paris Cedex 05, France. (Laurence.galoisy@impmc.upmc.fr)

Iron has long been known to play an important role in determining the properties of natural magmatic liquids. The determination of the sites occupied by ferrous and ferric cations in natural glasses may provide information on the physico-chemical conditions prevailing at the magmatic stage as well as on the cooling conditions of the magma. We discuss the spectroscopic data obtained on the Fe environment in calc-alkaline rhyolitic glasses (obsidians) from various localities, at the light of transmission electron microscopic observations. Fe2+ and Fe3+ ions partly occur within the glass structure, as indicated by XANES [1]. EPR and optical absorption spectroscopy (OAS). OAS reveals that some Fe2+ occurs in a regular octahedral site, an unusual environment in glasses.

Fe2+ and Fe3+ ions partly occur within the glass structure, as indicated by XANES [1]. EPR and optical absorption spectroscopy (OAS). OAS reveals that some Fe2+ occurs in a regular octahedral site, an unusual environment in glasses.

Specific absorption bands, assigned to Fe-Fe and Fe-Ti intervalence charge transfers (IVCT), are characterized by a spectacular intensity enhancement at low temperature (10K). This thermally-activated behavior shows an activation energy similar to that observed for IVCT in various minerals. The evidence of specific Fe2+ sites and of IVCT processes, indicate the presence of Fe-oxide clusters. These clusters, showing a local re-arrangement around Fe, are related to the cooling history of the glass, as they are not found in synthetic glasses [2]. They may be also precursors of the amorphous and crystalline Fe-oxides (Ti-magnetite and magnetite), 5-10 nm large, evidenced using TEM. The existence of these clusters and their nature seem to be related to the conditions of formation of the investigated obsidians and they may obscure the information brought by these glasses about its magmatic history.

Looking for PON in fluvial and marine sediments: Insights from nitrogen isotopic compositions

A. GALY1,*, R. G. HILTON2, N. HOVIUS1, J. SMITH1 AND R. B. SPARKES1
1Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK (*correspondence: albert00@esc.cam.ac.uk)
2Department of Geography, Durham University, Science Laboratories, South Road, Durham, DH1 3LE, UK

Processes involved in the cycling of organic matter can be preserved in sediments and recent studies have unravelled the importance of the erosion of the continents to the global organic carbon transfer [1-3]. The significance of such transfer to the biogeochemical cycles of other chemical elements associated to the organic matter (H, N, O, P, S, …) is, however, hampered by the small (<1%) abundance of particulate organic carbon in sediments transported by river in active margins and the occurrence of inorganic phases. This is particularly the case when N is considered since nitrate particulate deposition and ammonium in phyllosilicate can both be present in sediments. Here, we present case studies from modern systems investigating soil and river sediments from Taiwan and the Swiss Alps with modern marine clastic sediments from Taiwan and their Cenozoic analogue from the foreland basins of the Alps and the Pyrenees. Sediments have been decarbonated using hydrochloric acid and the decarbonatation process can have a significant impact on the N-isotopic composition, depending on how well lithified the sediments are. However, variations in the isotopic composition of bulk soils and common plant species are correlated in the tropical mountain forest of Taiwan. This suggests that the physical erosion of fixed-N in organic debris can be significant for the N cycle in vegetated active mountains belts. It also suggests an accurate quantification of the particulate organic nitrogen (PON) in these types of material [4]. The offset of ~4 permil between soil PON and standing biomass can be a powerful tool to distinguish erosional regimes where the erosion of the vegetation is insignificant (Swiss Alps) or not (Taiwan).


Speciation of trace elements in Strengbach soil solutions by ultrafiltration

S. GANGLOFF*, P. STILLE AND F. CHABAUX
LHYGES – UMR7517 1rue Blessig – 67084 Strasbourg, France (* sgangloff@unistra.fr, pstille@unistra.fr, francois.chabaux@eost.u-strasbg.fr )

This study deals with colloidal phases of soil solutions collected in the Strengbach watershed (OHGE). These solutions carry the chemical elements in the first meter of soil. The sampling has been performed below spruce at different depths (-5cm, -10cm, -30cm and -60cm) of a brown acidic to ochreous podzolic soil with help of lysimetric plates. The colloidal phase has been studied by frontal filtrations (1µm, 0,45µm and 0,22µm) and tangential ultra-filtrations (300kDa, 30kDa, 10kDa and 5kDa). Then, the initial solution, the different permeates and retentates have been analyzed for major, trace element and Dissolved Organic Carbon (DOC) concentrations.

The study elucidates the behavior of the different chemical elements in the various colloidal fractions separated from the soil solutions. The retention rate, derived during the ultrafiltration experiment, allows determining the proportion of each element in different forms, i.e. proportions in dissolved form and in the different colloidal fractions. The comparison of each element with DOC indicates that only some of the elements are correlated with DOC. Among the latter, it is possible to distinguish two elemental groups showing different behaviors: those correlated only with DOC and those correlated with DOC and another secondary phase such as iron oxy-hydroxides. The mass balance of the ultra-filtrations showed that in the >1µm filtrates some elements (REE, PO43-, Pb, Fe, Al) occur as precipitates, as colloids or as dissolved phase. The precipitates contain among others secondary minerals fluorencite and pyromorphite. The formation of these minerals occurs below 5 cm depth.

The ultra-filtrations of samples taken at different depths of the soil profile indicate that the chemical compositions of the colloidal fractions change in function of depth. Such depth variations may point to indicate the occurrence of different levels of colloid formation in these soil solutions.
Climate-carbon cycle feedback during glacial cycles

A. GANOPOLSKI1*, V. BROVKIN2, R. CALOV1, D. ARCHER3 AND G. MUNHOVEN4

1 PIK, Potsdam, 14412, Germany
2 MPI-M, Hamburg, Germany (victor.brovkin@zmaw.de)
3 University of Chicago, Chicago, 60637, IL, USA
(d-archer@uchicago.edu)
4 University of Liège, B-4000 Liège, Belgium
(guy.munhoven@ulg.ac.be)

Paleoclimate records reveal a close link between global ice volume and atmospheric CO2 concentration, at least, through the last 800,000 years. Despite many efforts over the last two decades, mechanisms of glacial-interglacial CO2 variability and its role for the glacial cycles remain elusive. Here using the Earth system model of intermediate complexity CLIMBER-2 which includes all major components of the Earth system – atmosphere, ocean, land surface, ice sheets, terrestrial biota, eolian dust and marine biogeochemistry – we performed simulations of the last glacial cycles employing variations in the Earth’s orbital parameters as the only prescribed climatic forcing.

In the experiments with constant CO2 concentration, temporal dynamics of the simulated glacial cycles strongly depend on the CO2 level. For CO2 concentrations about and above preindustrial one, the model simulates only short glacial cycles with precessional and obliquity frequencies. However, for lower CO2 concentrations the model simulates long glacial cycles with dominant 100 kyr periodicity. Simulated glacial cycles agreed favorably with paleoclimatic reconstructions, but their amplitude is underestimated compared to those of the simulations with time-dependent CO2 concentration. These results confirm that the positive climate-carbon cycle feedback plays an important role in amplification of long glacial cycles. Experiments with fully interactive CO2 shed some light on the mechanism of climate-carbon cycle feedback during glacial cycles. Forced by orbital variations only, the model is able to reproduce the main features of CO2 changes: the 40 ppmv CO2 drop during glacial inception, the minimum concentration at the last glacial maximum being 80 ppmv lower than the Holocene value, and the relatively abrupt CO2 rise during the deglaciation. The main drivers of atmospheric CO2 evolve with time: changes in sea surface temperature and volume of bottom water of southern origin exert CO2 control during glacial inception and deglaciation, while changes in carbonate chemistry and marine biology are dominant during the first and second parts of the glacial cycles, respectively.

Evaluation of marine primary organic aerosol emission schemes

BRETT GANTT*, MATTHEW JOHNSON AND NICHolas MeksHiDZE

North Carolina State University, Raleigh, NC, USA
(∗correspondence: bgantt@ncsu.edu)

In the last decade, there has been an increase in research concerning primary organic aerosol (POA) emissions from the ocean. Global source of ocean-emitted POA has been shown to be comparable to primary organic carbon particles emitted from combustion [1] and are sometimes found in concentrations more typical of organic aerosols in urban areas [2]. Due to their importance, several attempts have been made to better quantify the emission rate of marine POA for use in air quality and global climate models. In this work, we present results from the chemical transport model GEOS-Chem in which five distinct emissions schemes [1, 3, 4, 5, 6] of marine POA are implemented using a consistent sea spray function and chlorophyll-a concentrations ([Chl-a]). Model simulations are evaluated against long- and short-term observations collected in multiple coastal sites.

Calculations show that these schemes emit marine POA at different magnitudes and have distinct temporal/spatial distributions. Three of the emission schemes [3, 4, 5] are strongly tied to the wind speed dependence of the sea spray function and to a much lesser extent the [Chl-a]. On the other hand, the Spracklen et al. [1] emission scheme is primarily driven by [Chl-a] and is insensitive to surface wind speed. Between these two extremes is the Gantt et al. [6] scheme, which is affected by both wind speed and [Chl-a].

Preliminary results show that the emission schemes with strong wind speed dependence overpredicted concentrations in the winter relative to the summer at sites in the Northern Atlantic and Southern Ocean [7, 8]. The high organic concentration episode at Mace Head [2] was not reproduced well by any scheme, although the emissions with wind speed dependence outperformed the emissions based solely on [Chl-a]. This study shows that large uncertainty in marine POA emissions exists and requires further evaluation.


Goldschmidt Conference Abstracts 887
Mechanism of water–rock interaction of alkaline leaching uranium in Shihongtan deposit

B. GAO1,2 * AND Z. X. SUN1,2

1School of Civil and Environmental Engineering, East China Institute of Technology, Fuzhou 344000, China
(*correspondence: gaobai2007@sohu.com)
2Key Laboratory of Radioactive Geology and Exploration Technology Fundamental Science for National Defense Fuzhou, Jiangxi, 344000, China

The saturation index of sulphate and carbonate in groundwater of Shihongtan uranium deposit in Xinjiang has been calculated by geochemical model PHREEQC (table 1).

Table 1: The calculated results of saturation index of mineral.

<table>
<thead>
<tr>
<th></th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Anhydrite</th>
<th>Gypsum</th>
<th>Uraninite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sat Index</td>
<td>0.75</td>
<td>1.44</td>
<td>0.04</td>
<td>0.30</td>
<td>-6.34</td>
</tr>
<tr>
<td></td>
<td>-1.30</td>
<td>-2.76</td>
<td>-0.81</td>
<td>-0.60</td>
<td>-2.76</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>-0.17</td>
<td>-0.77</td>
<td>-0.56</td>
<td>-3.71</td>
</tr>
<tr>
<td></td>
<td>-0.23</td>
<td>-0.49</td>
<td>-1.56</td>
<td>-1.35</td>
<td>-5.69</td>
</tr>
<tr>
<td></td>
<td>-0.51</td>
<td>-0.37</td>
<td>-0.97</td>
<td>-0.66</td>
<td>-3.15</td>
</tr>
</tbody>
</table>

The results indicate that mining of the deposit is a difficult task by traditional acid or alkaline in situ leaching. Experimental researches of laboratory and field show that mining the uranium deposit is possible because of avoidance of precipitation of calcium sulphate and calcium carbonate in the aquifer, if the total dissolved solids of groundwater were diluted less than 3.45 g/L[1]. The uranium leaching is controlled by species of uranium mineral with study of electron probe. The uranium associated with kaolin or in between the grains of minerals is easier to be leached out than those associated pyrite or encompassed by the minerals[2]. Experimental researches show that more time of leaching, higher content of Ca2+ in recovery solution because of calcic mineral dissolution in uranium or and wall rock. The precipitation jam of calcium carbonate during in situ leaching will come into being because of reducing the liminal value of HCO₃⁻ content.

The study was supported by the project of the National Natural Science Foundation of China(40872165) and Science Bureau of Jiangxi Province (2009AF00100).


Geochemical characteristics of trace elements of sandstone-type uranium deposits in the Ordos Basin

E.G. GAO, S.G. HE* AND S.C. SUN

Institute of Disaster Prevention Science & Technology, Yanjiiao 101601, Beijing, China (grg@ustc.edu.cn)

The Ordos basin is the second largest sedimentary basins in China, as called Shan-Gan-Ning basin, and its main body area is 2.5×10⁵ square kilometers. The Yimeng Uplift in the north, the WeiBei Uplift in the south, the West Fold and Fault Belt in the west, and the Western Shanxi Flexure Belt in the east form a particular structure pattern. The Ordos basin is enriched with many energy resources and deposits [1-3], therefore, it has profound scientific sense and industrial value. Recent exploitation indicates that the sandstone-type uranium mineralization has economic value in this basin [4], it becomes the hotspot in the uranium exploration in China.

High precision ICP-MS was hired to study trace elements and REE from sandstone-type uranium deposit in the Ordos Basin, Northwestern China. We focus on the mechanism of uranium enrichments so that to present basis for further exploration. Results of total REE ranges from 30.3 to 713.4µg/g, REE distribution patterns of the sandstone-type uranium samples is light REE enriched and high REE depleted. Our study shows that high Y abundance and abnormity of Eu between 0.70~1.92, results show that U abundances are 0.73~150%g/g showing strong correlation between U enrichments and the related elements such as Ti, V, Zr, Mo and Au. In addition, thorium enrichments in most samples are correlated with ΣREE with some accordance of former study [5,6].

This study is supported by Teacher Foundation of China Earthquake Administration(No: 20090112)

Extensive N-loss from permeable Wadden Sea sediments due to aerobic denitrification

H. GAO, A. KHALILI, D. DE BEER, G. LAVIK AND M.M.M. KUYPERS*
Max Planck Institute for Marine Microbiology, 28359 Bremen, Germany
(*correspondence: mkuypers@mpi-bremen.de)

The role of permeable sediments in the oceanic N-budget is poorly understood. In this study, nitrogen (N) loss rates were determined in permeable sediments of the Wadden Sea using a combination of stable N isotopes, microsensor measurements and model simulation approaches. Results indicate that permeable Janssand sediments are characterized by some of the highest denitrification rates in the marine environment. Moreover, several lines of evidence showed that denitrification occurred under oxic conditions. N loss rates generally showed little temporal and spatial variation (207 ± 30 μmol m⁻² h⁻¹) over the three field campaigns conducted in autumn 2006 and spring and summer 2007. Utilizing an extensive time series of nutrient concentrations and current velocities obtained from a continuous monitoring station, NO₃⁻ flux into the sediment was modeled over a full annual cycle. Modeled NO₃⁻ fluxes were sufficiently high to support the experimentally derived N-loss rates. Combining the measured rates with the modeled results, an annual N-removal rate of 745 ± 109 mmol N m⁻² y⁻¹ was estimated for permeable sediments of the Wadden Sea. This rate agrees well with previous N loss estimates for the Wadden Sea based on N budget calculations. Our results indicate that permeable sediments, accounting for 58-70 % of the continental shelf area, are an important N-sink and their contribution to the global N-loss budget should be reevaluated.

Applications of laser microprobe analysis for silicon and oxygen isotopes (Fujian, China)

J.F. GAO AND T.P. DING
The Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources; Chinese Academy of Geological Sciences, Beijing 100037, China.
(correspondence: tony_and_mary@126.com)

The O and Si isotope compositions of minerals from the miarolitic cavity granite and pegmatite in Yunxiao county, Fujian province are measured by using conventional method and laser probe analytic method for determining their material sources and forming conditions. The results are listed in the Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ¹⁸OQUAL (‰)</th>
<th>δ³⁰SAMS-28 (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>Fs</td>
<td>Gar</td>
</tr>
<tr>
<td>Gr-01</td>
<td>7.6</td>
<td>6.4</td>
</tr>
<tr>
<td>Gr-02</td>
<td>8.0</td>
<td>5.6</td>
</tr>
<tr>
<td>Peg-01</td>
<td>7.7</td>
<td>6.3</td>
</tr>
<tr>
<td>Peg-02</td>
<td>7.4</td>
<td>5.6</td>
</tr>
<tr>
<td>Peg-03</td>
<td>7.7</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Table 1: The results of oxygen and silicon isotope compositions

*minerals were analyzed by using laser probe isotope analytic method. Q-quartz; Fs-feldspar; Gar-garnet.

The O and Si isotope compositions of quartz and feldspar from the pegmatite are very similar to those of the granite, indicating that they have the same magma source. From the oxygen isotope fractionation between quartz and feldspar, a temperature of 461°C is obtained for the granite, indicating that the granite may be subjected some extent of water-rock interaction after crystallization. This is consistent with the extensive development of pegmatite miarolitic cavity in granite. From the oxygen isotope fractionation between quartz and feldspar, a temperature range between 505°C and 532°C is obtained for pegmatite, indicating that fluid temperature was more than 500°C when the pegmatite was formed.

The silicon and oxygen isotopic ratios of garnet were both significantly lower than those of coexisting quartz and feldspar in miarolitic cavity, indicating that parallel silicon and oxygen isotopic fractionations are present between garnet and quartz (and feldspar), although the extent of silicon isotopic fractionation is smaller than those of oxygen isotope fractionation.
Quasi-simultaneous observation of currents, salinity and nutrients in the Changjiang plume on the tidal timescale

L. GAO* AND D.J. LI

State Key Laboratory of Estuarine and Coastal Research, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China
(*correspondence: lgao@sklec.ecnu.edu.cn)

During both the spring- and the neap-tide periods of November 2005, quasi-simultaneous observations were carried out by six boats over 26 h at 12 stations in the Changjiang plume. The simultaneous observations provided the actual distribution isopleths of salinity and nutrients that displayed considerable intra-tidal variations at surface, especially in the southeastern section of the study area (Figure 1). The lack of synopticity in sampling might lead to large discrepancies of the interpolated contours of salinity from the actual distribution isopleths. No clear flood-ebb asymmetry of salinity stratification was observed; whereas at inner stations, surface-to-bottom bulk velocity difference always tended to be greater during the ebb fraction of a semidiurnal cycle. At a given station, the weaker neap tides commonly induced stronger salinity stratification, less intra-tidal variability of salinity and nutrients, and less intrusion of bottom saltwater. Nutrients showed more nonconservative behaviors during the neap tides, presumably as a result of the prolonged residence time of seawater and decreased suspended particulate matter levels than during the spring tides.

This study was jointly funded by Ministry of Science and Technology of China (2010Cb951203), Shanghai Municipality (10JC1404400) and State Key Laboratory of Estuarine and Coastal Research of China (2009KYYW03).

Study on endocrine disrupting chemicals removal features in pingshantou waterplant of Huainan City, China

LIANGMIN GAO* AND GUIRONG SU

School of Earth and Environment, An Hui University of Science and Technology, Huainan 232001, China
(*correspondence: gaolmin@163.com)

Using a method for solid-phase extraction concentrated and high performance liquid chromatography analysis, detected the EDCs content of different water treatment process in pingshantou waterplan of Huainan city, researched the distribution characteristics and removal efficiency of EDCs in different water treatment process. The research results are as follows: DMP and DEP could be removed by rate of 100%, but BBPD, EE2, E1, BPA and NP were detected in different water treatment process, the detection rate was 100%. While the content of DMP, BBP, DBP, BPA increased in water treatment process. The content of BBP, DBP, EE2, BPA increased after pipe delivering. Conclusions: Conventional drinking water treatment process of EDCs removal is very limited; There are no rule to follow with EDCs in coagulation-sedimentation and chlorination process, the reasons may be: degradation products and secondary pollution were produced in processing process, which caused the content of BBP, DBP elevated in coagulation-sedimentation and chlorination process; And several byproducts of BPA and NP were found in chlorination. In addition, the impact of pollution substances exudated from conveying water pipe on EDCs should not be ignored.

Figure 1: Comparison between the snapshot distribution isopleths of salinity at surface on the two occasions of 12:00 (solid black lines) and 18:00 on November 2 (dashed blue lines) during the spring-tide survey. The two occasions are roughly regarded as the peak high- and peak low-tide phases for the entire survey region.
Fluorescence spectrum characteristic of the extractable humus in soil from Shannan developed area

LIANGMIN GAO* AND QINQIN ZHANG
School of Earth and Environment, An Hui University of Science and technology, Huainan 232001, China
(*correspondence: gaolmin@163.com)

Humus is a kind of amorphous, brown or brownish black, hydrophilic, acidic, polydispersed organic matter and more dispersed widely in soil, sediment, and water (such as lakes, rivers, oceans and groundwater, etc.). It is not only a major source of soil nutrients but also has a significant impact to physical, chemical and biological properties of soil, it is one of the indicators of soil fertility.

Contents of extracted humus in soil planted with different crops were determined, and the fluorescence spectra features of extracted humus in the same sampling point in different soil layers were analyzed. The results showed that contents of extracted humus in soil planted with different crops are different, there is no obvious rule. For different soil layers of the same sampling point, the distribution of extracted humus is not the same, mostly show that: the surface (0~20cm)> the middle (40~60cm)> the lower (80~100cm). The excited state fluorescence spectra of extracted humus in soil of different land types have similar fluorescence characteristics, peak obvious presents in about 390nm and 455nm. The fluorescence emission spectra are all broadband peak without obvious features. emission wavelength is about 500nm. The stimulate spectra of extractable humus in cotton soils has two distinct peaks around 445nm and 460nm, with the deepening of soil the two peaks separate more obviously. And extractable humus in surface layer, middle layer and lower layer has inspired fluorescence peak in 503nm, 498nm and 492nm in turn, peak type is moderate, and along with the increase of soil depth, fluorescence intensity greatly increase.

Geochemical and U-Pb age constraints on the occurrence of polygenetic titanites in UHP metagranite in the Dabie orogen

X.-Y. GAO*, Y.-F. ZHENG1, Y.-X. CHEN1 AND J.L. GUO2
1CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China (*correspondence: gaoying@ustc.edu.cn)
2State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China

Accessory minerals such as zircon and titanite are common in continental subduction-zone metamorphic rocks, and time and process of their formation can be dated by the U-Pb method and geochemical tracers. This is a great advantage to identify their genesis with respect to the origin of host rocks. Magmatic titanite was identified in the core of a few titanite grains with the overgrown rim of metamorphic titanite in UHP metagranite in the Dabie orogen. LA-ICPMS U-Pb dating gave Neoproterozoic ages for the magmatic titanite but Triassic ages for the metamorphic titanite. The magmatic and metamorphic titanites are clearly distinguished by differences in petrological and geochemical compositions. The magmatic titanite occurs as residual cores that show bright BSE, the presence of allanite and quartz inclusions, low contents of CaO, Al2O3 and TiO2 but high contents of Fe2O3 and MgO. In trace elements, the magmatic titanite exhibits high REE and HFSE contents, distinctly negative Eu anomalies with flat MREE-HREE patterns, and high Th/U ratios. In contrast, the metamorphic titanite occurs as rims and grains of homogeneously dark BSE that contain inclusions of epidote, quartz, K-feldspar, rutile, biotite and phengite, and have relatively high contents of CaO, Al2O3 and TiO2, but low contents of Fe2O3 and MgO, and relatively low REE and HFSE contents, slightly negative Eu anomalies with HREE depletion relative to MREE, and low Th/U ratios. The Zr-in-titanite thermometry yields 727 to 877°C at 0.5 to 1.0 GPa for the magmatic titanite, and 729 to 870°C at 1.5 to 2.0 GPa for the metamorphic titanite. The Neoproterozoic U-Pb chronometric system of magmatic titanite survived the Triassic continental subduction-zone HP-UHP metamorphism. This suggests a relatively high closure temperature of >800°C for the titanite U-Pb system. The metamorphic titanite is principally a product of retrograde metamorphism during decompression exhumation at the transition from HP eclogite-facies to amphibolite-facies. Therefore, titanite holds a great potential to petrology and geochemistry of continental subduction-zone processes.
Effect of phosphate fertilizer on the mobility of arsenic in fairdpur soil, central Bangladesh  

X.B. GAO1, Y.X. WANG1,*, Q.H. HU2 AND T. MA1  
1School of Environmental Studies and MOE Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, 430074 P. R. China  
(Xubo.gao@cug@gmail.com; *correspondence: YX.Wang@cug.edu.cn; Tengma@cug.edu.cn)  
2Department of Earth and Environmental Science, The University of Texas at Arlington, Arlington, TX 76010  
(maxhu@uta.edu)  

Effects of long term using of phosphate fertilizer on the mobilization of arsenic from soils have been seldom studied. In this study, the effects were investigated by column experiments using surface soil samples collected from fairdpur, central Bangladesh, an area with high arsenic presence in groundwater. A solution of 160 mg/L Ca(NO3)2 was first applied to the fully-saturate columns packed with soils to establish the stable As concentration in the effluent, and followed by leaching with phosphate fertilizer solution (represented with 10 mg/L Na2HPO4). An increase in the arsenic concentration in the effluent was observed after the Ca(NO3)2 input solution was replaced with either Na2HPO4 solutions. Dissolution of soluble arsenic-bearing minerals in the sediment with a rapid release of As, major cations, Fe, Mn, and Si was observed in the first hour. During the leaching period, there is no significant increase of As(III)/As(V) ratios in the effluent due to the oxic conditions in the experiment. Desorption of As from oxyhydroxide sorbents by phosphate is one of the major factors responsible for the elevated As concentration observed in the effluent [1, 2]. During the leaching periods of Na2HPO4, sodium mole percentage, as well as Na+/Ca2+ and Na+/Mg2+ ratios, of the effluent increased, probably due to aggregate breakdown, colloidal dispersion and mobilization in the columns, while an increase in Fe and Mn contents of the effluent may result from the release of particulate Fe and Mn oxyhydroxides. In addition, complexation of particulate arsenic with Fe/Mn oxyhydroxides may account for a significant portion of the enhanced arsenic concentration in the effluent.  


LA-ICP-MS zircon U-Pb geochronology of granites and its geological implication in the Baiganhu W-Sn deposit, NW China  

YONG-BAO GAO1,2,*, WEN-YUAN LI1 AND ZHAO-WEI ZHANG1,2  
1Xi’an Center of Geological Survey, CGS, Xi’an, Shaanxi 710054, China  
2Chang’an University, Xi’an, Shaanxi 710054, China  
(*correspondence: gaoyongbao2006@126.com)  

Baiganhu W-Sn deposit is a new found large W-Sn deposit in Qimantge, NW China, and W-Sn mineralization is closely related to the tonalite and monzonite granite, both of which belong to S-type granites. However, because of lacking of precise isotopic dating, the metallogenic epoch of Baiganhu W-Sn deposit is disputed. This paper provides the LA-ICP-MS zircon U-Pb isotopic dating result of the tonalite (BKN-01) and monzonite granite (BKN-03) from the Baiganhu deposit and discusses its geological significance. The CL images of zircons in the granites show most of the zircons present the typical characteristics of magmatic zircons with zoning structures. The LA-ICP-MS Zircon U-Pb isotopic dating show that the weighted mean 206Pb/238U ages of tonalite and monzonite granite are 429.5±3.2 Ma (MSWD = 0.0026), and 430.5±1.2 Ma (MSWD = 0.0111) respectively. Both of the ages are concordant (Fig.1), and they can represent the petrogenic ages of the granites. Therefore, this paper proposed that the S-type granites in Caledonian period, which were formed by the melting of sedimentary strata, are closely related with forming of W-Sn in Baiganhu deposit. These findings are of great significance in further research on the formation environment of Baiganhu W-Sn deposit, and guiding the ore prospecting directions.  


Figure 1: U-Pb concordia diagram of zircons of granites in the Baiganhu W-Sn deposit, Qimantge, NW China.  

This study was supported by China Geological Survey project (No. 1212010911032, 1212011121088 and 1212011121092)
Geochemistry, paleoenvironment and timing of Lower Aptian organic rich beds of Paja Formation (Eastern Cordillera, Colombia)

TATIANA GAONA-NARVAEZ1*, FLORENTIN J.-M.R. MAURRASSE1, FERNANDO ETAYO-SERNA2 AND CARRIE REBENACK1

1Dept. of Earth and Env., Florida Int. Univ. 11200 S.W. 8th Street, Miami, FL 33199, USA (*correspondence: tgaon001@fiu.edu; maurrass@fiu.edu, crebe001@fiu.edu)
2Inst. Colombiano de Geología y Minería, INGEOMINAS, Diagonal 53 # 34-53, Bogotá, Colombia (fetayos@gmail.com)

Lower Aptian organic-rich marine sediments are interpreted with respect to anoxic episode, “Oceanic Anoxic Event 1a” (OAE-1a), coeval with δ13C segments C3 to C6, of duration between 1.0 and 1.3 MA [1,2].

A 115m section of the Lower Aptian Arcillolitas Abigarradas Member of the Paja Fm at Villa de Leiva (Tunja-Villa de Leiva road) includes a prominent 4m-thick interval of black shale 10 meters below the base of the lowest Upper Aptian (Gargasian) Dufrenoyia sanctorum-Stoyanoviceras treffryanus ammonite assemblage zone [3]. Similarly, at the Curití Quarry (San Gil-Curití road), a 12m section includes 8m-thick organic-rich shale at the base of the Paja Fm, which overlies Barremian-age carbonate ramp deposits of the Rosablanca Fm. The base of the Paja Fm yielded reworked and phosphatized middle Barremian to lowest Aptian ammonites: Pulchellia, Gerhardtia, Toxancycloceras, Karsteniceras and Prodeshayesites. High-resolution analyses of these sections, including TIC (wt% CaCO3), TOC (wt% C), and stable carbon isotope values (δ13Corg), characterize the stratigraphic relationship of these organic-rich levels of the Paja Fm and OAE-1a.

At Villa de Leiva, the organic-rich interval includes laminae associated with gypsum, pyritic concretions, absence of bioturbation and benthic fossils, and yielded increased TOC values (1.17% to 5.33%). These sediments accumulated under anoxic conditions in a subtidal, hypersaline environment [4]. C- isotope data show δ13Corg values from -19.79‰ to -24.65‰. At Curití, the organic-rich sediments are devoid of benthic fossils and bioturbation, and TOC values are up to 8.4%, also indicative of oxygen-depleted conditions. C- isotope data yielded δ13Corg values between -22.05‰ and -24.65‰. In both sections the range of δ13Corg values, and the trend of the δ13Corg curve are compatible with the Lower Aptian interval C7 [1, 2]. Therefore, both organic-rich intervals of the Paja Fm are subsequent to OAE-1a, which is known to occur between isotopic levels C3 and C6.

Beach placer, a proxy for the average Nd-Hf isotopic composition of a continental area

M. GARCON*, C. CHAUVEL AND S. BUREAU
ISTerre, BP 53, 38041 Grenoble Cedex 9, France (*correspondence: marion.garcon@ujf-grenoble.fr)

Beach placer deposits concentrate detrital heavy minerals which are the erosion products of large areas of continental crust. Here, we report the first analyses of Nd-Hf isotopic ratios and trace element concentrations that we measured in a beach placer from Camargue, France and in its pure mineral separates. Both the bulk composition of the placer and those of its pure mineral separates were determined. We also report mineral proportions obtained using observations under a binocular microscope and X-ray microfluorescence cartography.

Our results indicate that monazite totally controls the placer Nd isotopic composition (ENd = -9.3) while zircon dominates its Hf isotopes (Eh = -13.0) even though both mineral phases represent only a small proportion of the heavy mineral assemblage (3.5% and 10% respectively). We demonstrate that the Camargue placer provides a good estimate of the average Nd and Hf isotopic composition of the continental area drained by the Rhone River in western Europe (ENd = -9 and Eh = -13). Using these values, we calculate two-stages model ages and show that almost all the placer minerals are derived from Proterozoic crustal protoliths. This provides valuable information on the history of the continental crust drained by the Rhone River. In particular, it suggests that little juvenile crust was created during the recent geological events that formed the Alps and the Massif Central, the two main massifs from which the placer minerals originate.

More generally, we propose that similar measurements made on other worldwide beach placer deposits could provide estimates of the present-day Nd and Hf isotopic composition of large continental areas, values that are difficult to obtain due to the well-known heterogeneity of continental material but are essential to model the growth of continental crust through Earth history or to model the impact of crustal material when recycled into the mantle.

Analysis of geochemical “twins”
Al/Ga and Si/Ge in rock-forming silicate minerals in granitoids using LA-ICP-MS

N. GARDENOVÁ1*, V. KANICKÝ1, K. BREITER2, AND T. VACULOVÍC1
1Department of Analytical Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic (*correspondence: 369148@mail.muni.cz)
2Institute of Geology, Academy of Science ČR, Praha

The aim of this study is to determine ratios of Al/Ga and Si/Ge in natural silicate minerals from different types of granitoids from Bohemian massif and compare these ratios with elemental ratios commonly used in geochemistry like K/Rb, Nb/Ta and Zr/Hf. All these ratios represent (i) different source lithology (metasedimentary or metagneous rocks, subduced slab, metasomatised lower crust) of granitic melts, (ii) evolution via fractional crystallisation, mixing, reaction with fluid etc., (iii) ability of particular crystal lattice of rock-forming minerals to preferentially accommodate Ga or Ge.

The presented results was obtained using three different methods – pneumatic nebulization with inductively coupled plasma mass spectrometry (PN-ICP-MS), laser ablation with ICP-MS (LA-ICP-MS) and electron probe microanalysis (EPMA). PN-ICP-MS was used for determination of whole content of the rock samples after fusion with LiBO2. LA-ICP-MS and EPMA was used for local microanalysis of individual grains of silicate minerals.

The first results show that of Al/Ga-ratio in analyzed rock is relatively stable (Al/100Ga ~5-15), whereas Si/100Ge-ratio during fractionation increased: in the Trebič pluton from about 80 in amphibole-biotite durbachites to 250-300 in late biotite durbachites, in orthogneisses from about 230 in biotite orthogneisses to about 380 in some of two-mica facies, in the Melechov pluton from about 150 in the Lipnice facies do about 400 in the Melechov facies. In the Podlesí granite system, the Ge- and Ga-contents are influenced by greisenisation: namely the Ga is during hydrothermal processes mobile and its content remarkably decreases (Al/Ga-ratio increase).

Laser-ablation analyses of individual silicate minerals from the Cínovec borehole showed, that Ga is preferentially concentrated namely in mica (zinnwaldite and protolithionite), and more in albite than in associated K-feldspar. Ge is namely concentrated in mica. Contents of both Ga and Ge in quartz are lower than their detection limits.

Production of superoxide and hydrogen peroxide on photolysis of natural organic matter

S. GARG1, A.L. ROSE1,2 AND T.D. WAITE1*
1School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW 2052, Australia (d.waite@unsw.edu.au)
2Southern Cross Geoscience, Southern Cross University, Lismore, NSW 2480, Australia

Irradiation of Suwannee River fulvic acid (SRFA) at pH 8.1 with simulated sunlight resulted in production of nanomolar concentrations of superoxide and hydrogen peroxide. Analysis of the results obtained confirmed that SRFA contains a redox-active chromophore which reduced oxygen to yield superoxide upon photoexcitation. Hydrogen peroxide was generated exclusively via uncatalysed disproportionation of superoxide produced in this way.

Superoxide decayed through both uncatalysed disproportionation and an oxidative pathway that did not result in hydrogen peroxide production, whereas hydrogen peroxide did not undergo further reaction to any discernible extent over the one-hour duration of irradiation. Singlet oxygen did not contribute substantially to production of superoxide or hydrogen peroxide, but was found to play a critical role in controlling the mechanism and associated rate of superoxide decay in the irradiated solution.

A kinetic model based on these observations is presented which provides an excellent description of the experimental results and is also consistent with observations from a wide range of other studies investigating various aspects of SRFA redox chemistry and photochemistry.
Dissolution of gold in hydrochloric acid

D. GARIJO* AND N. SHIKAZONO
Graduate School of Science and Technology, Keio University, Yokohama, 223-8522, Japan (*correspondence: garijodiego@gmail.com, sikazono@apple.keio.ac.jp)

The purpose of this work is to study hydrochloric acid as an alternative to cyanide for the dissolution of gold in the mining industry. The use of cyanide is controversial due to its toxicity. With hydrochloric acid the process would be safer for the environment and workers. J. D. Clemens showed that hydrogen gas can pass through Teflon at high temperature [1]. When dissolving gold in hydrochloric acid, several reactions should be taken into account:

\[
\begin{align*}
\text{Au} + H^+ + 2\text{Cl}^- & \rightarrow \text{AuCl}_2^- + 1/2\text{H}_2 \\
\text{Au} + 3H^+ + 4\text{Cl}^- & \rightarrow \text{AuCl}_4^- + 3/2\text{H}_2 \\
\text{Au} + 4H^+ + 4\text{Cl}^- & \rightarrow \text{HAuCl}_4 + 3/2\text{H}_2
\end{align*}
\]

The removal of H\textsubscript{2} in the system should quicken the process by forcing these reactions to proceed from left to right. Research by Nakata using Teflon vessels showed high gold concentrations compared to previous studies [2]. This is supposed to be due to degassing of H\textsubscript{2} from the system.

A proper combination of parameters will determine if the process is possible and economically viable. By now, it has been found that area of the gold particles, concentration of hydrochloric acid, temperature and time are the most relevant variables. The presence of amorphous phase can determine the speed of dissolulion in short time intervals. The manufacturing process, apart from creating amorphous phase as a result of mechanochemical reactions, may inject energy into the surface. If this energy is heterogeneously distributed, activated zones could be preferentially dissolved. Regarding the recycling of gold alloys, composition can be important. The nature of the vessel (Teflon, or other non-permeable) is not important when the experiment is very short (less than ten days).

[1] J. D. Clemens et al., Teflon as a Hydrogen Diffusion Membrane: Applications in Hydrothermal Experiments, 

Colloidal arsenic distribution and speciation in mine soils

F. GARRIDO¹, F. LABORDA¹, E. BOLEA¹, M. HELMHART¹
P. O’DAY² AND S. SERRANO¹

¹Institute for Agricultural Sciences (CSIC), Madrid (Spain)
²University of California, Merced, CA 95343 USA
³Institute of Environmental Sciences, University of Zaragoza, Zaragoza (Spain)

Arsenic associated with colloidal particles is an important vector for As migration in contaminated soils. Using Asymmetric-Flow Field-Flow Fractionation (AsFlFFF) coupled to an inductively coupled plasma-mass spectrometer (ICP-MS), we determined the As distribution as a function of the particle size of the colloidal fraction of soils samples. The samples were collected from stained preferential flow paths and bulk soil samples, impacted by a mine waste. Physical and chemical properties of the colloids were also determined using X-ray-diffraction, SEM and TEM. Arsenic and Fe speciation in the colloidal fraction was characterized using X-ray absorption (XAS) spectroscopy techniques.

Preliminary results indicated that more than 47% of the As mobilized in the preferential flow paths (70.5 mg/L) was associated with the colloidal fraction of the soil. Instead, 5% (2 mg/L) of the mobile As in the bulk samples of the soil was colloidal As. Common to both samples, a similar fractogram (1-1000 nm) was obtained for As, Fe and Al, suggesting an association of As with Fe and/or Al colloidal particles. As XAS analysis of the colloidal fractions (>10 nm) of the soil samples, indicated As adsorption on ferryhidrite as the main As-colloid retention mechanism. The presence of Fe-oxyhydroxides in addition to phyllosilicates was also showed by Fe X-ray absorption analysys. These results show the important role of Fe-oxyhydroxides as nanovectors of colloidal As in preferential flow paths and bulk samples of a contaminated soil.
Platinum group minerals (PGM) from chromitites of Kytlym Uralian-Alaskan type complex (Russia)

G. GARUTI1*, F. ZACCARINI1 AND E.V. PUSHKAREV2
1University of Leoben, Dept. Appl. Geol. Sci. Geophysics, Leoben, Austria
(*correspondence: giorgio.garuti@unileoben.ac.at)
2Ural Division of Russian Academy of Sciences, Inst. Geol. Geoch., Ekaterinburg
(mineresoc.org)

Several PGM have been found in two different types of chromitites associated with the Kytlym Uralian-Alaskan type complex (Northern Urals, Russia). Type-1 chromitite forms small schlieren or pods irregularly distributed in dunite, whereas the type-2 occurs as thin layers within amphibole-rich clinopyroxenite veins (Butyrin-veins) cutting across the dunite. Type 2 chromitite is enriched in Fe3+ and Ti compared to type 1. The concentration of IPGE (Os+Ir+Ru) decreases from 408-580 ppb in type-1 to 293 ppm in type-2. The latter also distinguishes for a much higher PPGE (Rh+Pt+Pd) content (22679 ppb) compared with type-1 (4776-10836 ppb), showing a Pd-Ir ratio of 151 in front of 0.6 in type-1. Alloys in the Pt-Fe-Ni system (isoferroplatinum tetraferroplatinum and ferronickelplatinum), erlichmanite, cuprorhodiste and osmium occur as primary polygonal inclusions in type-1 chromitite. Tulameenite is exclusively located along cracks in contact with secondary ferrian chromite, magnetite and chlorite, or constitutes the metasomatic replacement of primary Pt alloys. In contrast, the PGM assemblage of type-2 chromitite consists of Pd, Hg, Pt and Cu alloys (mainly potarite and Cu-rich potarite) and Pt-Fc-Cu with minor unnamed compounds of Rh-Te-Hg, Pt-Fe-Pd and Pd-Fe-Cu-S. With the exception of few Pt-Fe alloys that occur enclosed in fresh chromite, most of these PGM occur as irregular grains in the contact between chromite and silicates (clinopyroxene and amphibole), usually associated with pentlandite and pyrrhotite. Type-1 PGM precipitated in the high-temperature magmatic stage prior to or concomitant with chromite crystallization, under variable condition of S and O fugacities as well as Fe activity. Only tulameenite formed during low temperature, hydrothermal process. The composition and paragenetic assemblage indicates that PGM in type-2 chromitite derived from a more evolved melt (high Pd-Ir ratio) characterized by the activity of high-temperature fluids enriched in Hg, Te and Cu. The origin of this melt, i) last-stage fractionation of the same melt that generated the type-1 chromitite, or ii) fluid-rich melt derived from an external source, is still open to question.

Comparison of biomass used in Polish power-plants with other types of biomass

R. GASEK1*, W. WILCZYŃSKA-MICHALIK1 AND M. MICHALIK2
1Institute of Geography, Pedagogical University, ul. Podchorążych 2, 30-058 Kraków, Poland
(*correspondence: rgasek@ap.krakow.pl; wmichali@up.krakow.pl)
2Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Kraków, Poland
(mineresoc.org)

The aim of this study is to compare general characteristics of biomass used in energy production in Poland with other biomass types. We analyzed wood and woody biomass, agricultural straw, and agricultural biomass. Moisture content (as-received and air dried) is, respectively, within ranges of 5.4-26.2wt% and 1.2-1.6wt%. Ash yield (dry basis, 550°C) varies from 0.8 to 10.6wt%. Volatile matter (dry basis) content is between 72.3-84.8wt%. The C content in biomass is within the range 49.04-54.51wt% (daf – dry, ash-free basis); O content calculated by difference varies in the interval 37.32-43.26wt% (daf); H within the range of 5.58-6.35wt% (daf); N content is from 0.29-2.93wt% (daf); S content varies from 0.01 to 0.23wt% (daf). The Cl content measured in dry material varies from 0.017-0.253wt%.

Comparison of studied samples of biomass with published data (e.g. [1]) indicates that values of moisture, volatile matter content and ash yield are within relatively narrow range. Ash yield is relatively low in studied samples and volatile matter values are relatively high. The C content is relatively low in comparison with other types ob biomass. Oxygen content is rather high. The S, N and Cl contents are relatively low.

Changes in Neogene Himalayan erosion regime: Input of Pb and Nd isotopes into the Indian Ocean

J.C. GATTACCECA1*, A. GALY1, A. M. PIOTROWSKI1 AND M. FRANK2
1Dept. of Earth Sciences, University of Cambridge, CB2 3EQ Cambridge, UK (*correspondence: jcg54@cam.ac.uk) 2Leibniz Institute of Marine Sciences (IFM-GEOMAR), Wischhofstraße 1-3, 24148 Kiel, Germany

Pb- and Nd- isotopic time-series from the authigenic fraction of Central Indian Ocean sediments have been interpreted as responding to changes in the relative amount of Himalayan erosion during the Cenozoic [1,2]. Detrital records of Nd- and Sr- isotopes from the Bengal deep-sea fan suggest a source of sediment dominated by the High Himalaya Series (HHS) for the last 20 Ma [3,4]. Associated variations of Pb-isotopes are not known, and a more precise reconstruction is hampered by the lack of information about temporal changes in the isotopic composition of detrital Pb and Nd carried by rivers draining the Himalayas.

We present new Pb- and Nd-isotope time series, together with rare earth elements, from the bulk detrital and silt-sized fractions as well as the authigenic fraction of deep-sea sediment over the last 20 Ma from Ocean Drilling Program Sites 717 and 718 on the Bengal fan, along with Pb- and Nd-isotopic compositions of the bedloads of Himalayan rivers.

The oldest bulk detrital and silt-sized fraction samples (7-17 Ma) show similar and relatively uniform Pb- and Nd-isotopic compositions characteristic of a stable input from the HHS. The youngest samples (<1 Ma) show the same uniformity with a shift towards more radiogenic values, implying a greater contribution of the Lesser Himalaya Series. However, over the Pliocene (1-7 Ma), strongly marked shifts in both isotopes are observed, along with a decoupling between the bulk detrital and silt-sized fractions.

These results imply a strong variability in the erosion and weathering regime of the Himalaya over the Neogene, and we will discuss them in the context of tectonic and climatic changes. We will discuss as well the implications of these changes for the interpretation of the deep water evolution of these isotope systems in the Central Indian Ocean.


Black Reef and Witwatersrand Gold fingerprint, South Africa

C GAUERT1*, D BATCHELOR2, S FUCHS1,3 AND G KLOESS3
1Univ. of the Free State, RSA (*correspondence: Gauertcdk@ufs.ac.za) 2Karlsruhe Inst. f. Technologie, Inst. f. Synchrotronstrahlung 3Inst f. Mat Sc. & Crystal, University of Leipzig, Germany

The origin of the gold, the Uranium and the PGEs in the basal conglomerate of the palaeoproterozoic Black Reef Formation (BR) of the Transvaal Supergroup in South Africa is debated because of the economic significance of this gold ore body. The geochemical trace element fingerprint of the Gold is used to unravel the origin of the Black Reef Gold. Based on EMP, LA-ICP-MS and SR-μ-XRF measurements Black Reef and Witwatersrand (WR) gold can be distinguished by means of their different degree of true fineness, and the Hg, Cu, Fe, S, Ti and Ni trace element content. Among the elements which are correlatible with gold, Sn, Sb, Pb, and Pt, possibly in combination with Mn, Se, Pb, and Ir appear to be the most effective element distinction of gold sources due to their moderate iterative variation.

Figure 1: Synchrotron micro-XRF spectrum of BR and WR Gold, and pyrite and quartz at 30 keV energy.

The very similar heavy mineral content argues in favour of a reworked WR gold origin of the BR gold. Against a WR origin argues concretionary pyrite as major component and the less frequently occurring Ni-Co-Fe-sulpharsenides in the Witwatersrand reefs, however its frequent appearance in BR. The Gold in the BR at Consolidated Modderfontein Au Mine on the East Rand has a lower fineness, lower Hg and Cu content compared to WR gold, whereas Fe, S, Ti and Ni concentrations are higher. Compositions of WR gold from different localities, as well as greenstone-hosted gold will be used in the debate of an alternative source area for the BR gold from the East and West Rand areas.
Characterization of nanoparticulate arsenic in waters draining abandoned gold mine tailings

A.G. GAULT1*, M.B. PARSONS2 AND H.E. JAMIESON1

1Department of Geological Sciences and Geological Engineering, Queen’s University, Kingston, Ontario, K7L 3N6, Canada (*correspondance: gault@geol.queensu.ca)
2Natural Resources Canada, Geological Survey of Canada (Atlantic), 1 Challenger Drive, Dartmouth, Nova Scotia B2Y 4A2, Canada

Waters draining abandoned gold mine sites often contain elevated concentrations of As, however, relatively few studies have attempted to distinguish between colloidal As and truly dissolved As. This distinction is important since it impacts the mobility, bioavailability, and toxicity of As. We collected surface waters draining abandoned gold mine tailings in Nova Scotia, Canada and sequentially filtered them through standard 450 nm pore size filters followed by stirred cell ultrafiltration through 10 nm polycarbonate membranes. Arsenic concentrations in the <450 nm fraction, traditionally termed “dissolved”, ranged from 0.2 – 1.6 mg/L. Colloids, operationally defined here as suspended solids of 10 to 450 nm diameter, accounted for 5 – 56% of this As. SEM inspection of the 10 nm filters indicated that Fe and Ca were commonly associated with As-bearing nanoparticles. This was corroborated by synchrotron-based μXRF mapping which revealed that As was closely correlated with Fe, and to a lesser extent Ca. Multiple μXANES analyses indicated that arsenate was the dominant form of nanoparticulate As, with minor amounts of arsenite. These analyses showed no evidence for As-bearing sulfides, implying that arsenopyrite, the original mineralogical host of As prior to mining, was not a significant contributor to colloidal As. Synchrotron-based μXRD examination was hampered by the limited sample mass collected on the filter; however, akaganeite was found to be associated with As hotspots identified by μXRF mapping. Taken together, these preliminary data suggest the primary nanoparticulate vectors of As are secondary mineral assemblages such as hydrous (Ca-)Fe arsenates and Fe oxyhydroxides, previously shown to be major As-rich phases within the near-surface, weathered tailings at these historical gold mine sites [1].


Cadmium isotopic composition in cultured marine phytoplankton

M. GAULT-RINGOLD1,2*, R. STRZEPEK1,3, C. H. STIRLING1,2, R. D. FREW1 AND K. A. HUNTER1

1Dept. of Chemistry, Univ. of Otago, Dunedin, New Zealand (*correspondence: melaniegr@chemistry.otago.ac.nz)
2Center for Trace Element Analysis, Dunedin, New Zealand
3NIWA, Dunedin, New Zealand

Cadmium (Cd) has been used as a marine paleo-nutrient proxy [1] despite its complex and poorly understood biogeochemical cycling in the oceans. The past five years have seen an increasing interest in the stable isotopic composition of Cd in the marine environment as this information has the potential to be used as a tracer for the physical and biological controls of Cd cycling in the oceans and its use as a micronutrient. It has also been suggested that Cd isotopes themselves may be a reliable paleoproxy for primary productivity [2].

Both iron (Fe) and zinc (Zn) have been shown to influence the uptake of Cd in both cultured and natural phytoplankton populations [3]. Phytoplankton utilize Cd in the place of Zn for the enzyme carbonic anhydrase (CA) with some species expressing a Cd-specific CA enzyme when grown under Zn-limiting conditions [4].

Using multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) combined with double spiking techniques, significant 0.1%-level isotopic fractionation of Cd in seawater has been demonstrated and attributed to biological uptake [5]. Using these techniques, we examined the Cd isotopic fractionation associated with biological uptake in cultured marine phytoplankton under varying Fe and Zn-limiting conditions.

These experiments confirm that there is an isotopic fractionation associated with biological uptake of Cd, leaving the residual medium isotopically heavy. Fractionation factors calculated, assuming a Rayleigh distillation model, for these cultures demonstrate that Zn-limitation is influential in the resulting Cd isotopic compositions.

The importance of Zn bioavailability on Cd isotopic composition implies that the biogeochemical cycling of Cd in the oceans is complex, which calls into question the potential application of Cd stable isotopes as a paleonutrient proxy.

Water-rock interaction at the Theistareykir geothermal field in NE-Iceland

Bjarni Gautason1,* and Karlis Muehlenbachs2

1Iceland GeoSurvey & Univ. of Akureyri, P.O. Box 30, 602 Akureyri, Iceland (*correspondence: bg@isor.is)
2University of Alberta, Edmonton AB, T6G-2E3, Canada (karlis.muehlenbachs@ualberta.ca)

The Theistareykir volcanic system constitutes the western most part of the Northern Volcanic Zone (NVZ) in Iceland. Unlike its nearest neighbor to the east, the Krafla system, it does not have a well developed caldera structure. However, near the center of the system there are sporadic outcrops of siliceous rocks.

Bæjarfjall is a sub-glacial tuya located centrally in the system. On its northern slopes extensive acid sulfate alteration provides evidence for a vigorous geothermal system. To date six deep (~2 to 3 km) exploration wells have been drilled in the area. Cuttings from the wells record extensive alteration of the bedrock with epidote-chlorite (T ≥ 240°C) and amphibole-epidote (T ≥ 290°C) facies metamorphism recorded at relatively shallow depths. Temperature logging and modelling shows that the geothermal gradient in the area follows the boiling point curve in the uppermost 2.5 km.

We have separated cuttings from selected depths in well ThG-1, taking care to obtain only cuttings of the dominant lithology from each of the selected depth intervals. These cuttings have been analyzed for their 18O/16O ratios. The δ18O values of the rocks range from -4.0 to -10.2 ‰ (SMOW) recording extensive exchange with meteoric derived hydrothermal fluid and very high time-integrated water-rock ratios. A general trend of decreasing δ18O with depth is observed. From the data gathered to date it appears that most depleted rock occur close to presently active aquifers. More surprising however, is the depleted character (δ18O < -8.0 ‰SMOW) of apparently unaltered (basaltic) intrusives.

The overall characteristics of the profile (δ18O vs. depth) is similar to that obtained previously from the Krafla hydrothermal system [2].


Magnesite growth inhibition by organic ligands: Complexation and adsorption

Q. Gautier1,*, P. Benézeth1, G. Jordan2, U.-N. Berninger2 and J. Schott1

1 Géosciences et Environnement Toulouse (GET), CNRS, UMR 5563, 14 Avenue Edouard Belin, 31400 Toulouse, France (*correspondence: quentin.gautier@get.obs-mip.fr)
2 Dept. f. Geo- u. Umweltwissenschaften, Ludwig-Maximilians-Universität, 80333 München, Germany

Magnesite is object of scientific attention due to its potential for long-term CO2 sequestration. Organic ligands are widespread in natural environments, and because of their promoting effect on Mg-containing silicates dissolution, it has recently been suggested that some carboxylate ligands could be used to enhance ex situ mineral carbonation [1]. However, the influence of such organic ligands on magnesite precipitation still needs to be elucidated.

We performed macroscopic and microscopic crystal growth experiments using mixed-flow reactors (MFR) and Hydrothermal Atomic Force Microscopy (HAFM) at temperatures between 80 and 150°C and slightly alkaline conditions. Three model ligands were investigated for their different chemical and structural properties: oxalate, citrate and EDTA.

MFR experiments showed that at concentrations above 0.01 mM, the investigated ligands inhibited magnesite growth. Inhibition is positively correlated with the complexation of Mg2+ by the ligands. Furthermore, by precisely calculating saturation states, we show that citrate causes a reduction of the kinetic rate constant of magnesite growth: for instance, citrate concentrations as low as 0.2 mM induce a 4-fold decrease of the rate constant, an effect that is not observed for oxalate.

These results point towards different surface effects of the ligands.

HAFM observations showed that all three ligands interacted with steps on the magnesite surface, and modified the shape of growth islands. Measurements of step advancement rates suggest that citrate strongly inhibits growth at acute steps, which has been suggested to control magnesite growth at similar conditions [2].

Therefore at the investigated conditions, inhibition of magnesite growth by organic ligands appears to be a consequence of both Mg2+ complexation decreasing solution saturation, and specific interactions of the ligands at the magnesite surface. The results help to assess a potential use of organic ligands for mineral carbonation purposes and may improve our understanding of the long-term fate of CO2 in ligands-containing storage sites.

Magnetic susceptibility of Zafarghand granitoidic pluton
NEGAR GAVANJI*, M. SADEGHIAN AND S. SHEKARI
Shahrood University of Technology, Shahrood, Iran
(*correspondence: g.negar20@yahoo.com)

Zafarghand granitoidic pluton (ZGP) is located in the 160 km of NE Isfahan. This pluton is one of the granitoidic pluton of Orumieh Dokhtar structural zone and its lithological composition range includes: gabbro, diorite, granodiorite and granite. Eocene volcanic and volcano sedimentary are host rocks. This pluton investigated in the light of Anisotropy of Magnetic Susceptibility (AMS) method. 1008 samples were gotten from 123 stations in ZGP. Based on some criterias, magnetic parameters of these samples have been measured in the magnetic lab of Shahrood University of technology by MFK1-FA kappabridge machine. The measured mean magnetic susceptibility (Km in µSI) of the different rock groups are as follows: Gabbros (38120), diorites (26558), granodiorites (16922) and granites (9885). Based on these values gabbros and diorites have higher magnetic susceptibility [F.1].

Figure 1: Km- Lithology diagram

This characteristic confirmed by the presence of magnetite in polished sections, thermal magnetic diagrams and Geochemistry analyze. Km values which they are more than (500 µSI) indicate that studied granitoidic rocks are ferromagnetic and correlate with I-type granitoids [1, 2].


Highly siderophile element and Os isotope systematics of pyroxenite layers from the Lanzo peridotite body (Northern Italy)
T. GAWRONSKI* AND H. BECKER
Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstrasse 74–100, D-12249 Berlin, Germany
(*correspondence: gawronski@zedat.fu-berlin.de)

Mantle pyroxenites are believed to represent a minor constituent of the Earth’s mantle, but may yield insight into the origin, modification and transport of mafic magma. Mantle sources enriched in pyroxenite have been suggested as explanation for coupled suprachondritic 186Os/187Os signatures in some mantle plume sources [1, 2].

The spinel and plagioclase facies Lanzo peridotite body includes layers of spinel-and plagioclase-bearing websterite, clinopyroxenites and orthopyroxenites up to several dm in thickness. Abundances of highly siderophile elements (HSE) in the pyroxenites display no correlation with Al2O3, CaO and Na2O. Concentrations of Os, Ir, and Ru range from 1 to 0.01 x values in peridotites. Aluminum rich clinopyroxenites show enrichment of Pt, Pd, Au and Re over Os, Ir, and Rh, and initial γOs (200 Ma) of +25 to +150. Concentrations of Pt, Pd, Au and Re in such samples are only occasionally higher than estimates for primitive mantle values. Aluminum poor websterites are less depleted in Os, Ir, Ru, Rh and display less enrichment of incompatible HSE, with γOs (200 Ma) of -2 to +43, reflecting a smaller contribution from melt enriched in incompatible HSE. HSE ratios in the pyroxenites range from sub- to suprachondritic (Os/Ir:0.40-1.66, Ru/Ir:0.26-3.70, Rh/Ir:0.23-0.55, Pt/Ir:1.03-26.48, Pd/Ir:0.79-42.92, Au/Ir:0.26-3.75, Re/Ir:0.15-2.67, Pt/Re:1.96-151.30). Two samples (out of 12) with unusual composition display Pt/Re high enough to develop coupled suprachondritic 186Os/187Os with time as reported for some picrites and komatiites [2].

With the exception of 3 samples, most pyroxenites are correlated in a Re-Os isochron diagram and yield an isochron date of 1136±120 Ma (186Os/187Os = 0.13±0.01). This date is considerable older than the emplacement during the early Mesozoic (200 Ma) but coincides with a Sm-Nd model age of 1200 Ma for the southern Lanzo peridotite body [3].

Spatial distribution of erosion rates in small Tahitian catchment (10km²), from cosmogenic ³He in olivine

ERIC GAYER¹, FENGYIN YE² AND SUJOY MUKHOPADHYAY³

¹Institut de Physique du Globe de Paris, Sorbonne Paris Cité, UMR 7154 CNRS, 75005 Paris, France (egayer@ipgp.fr)
²Université de Polynésie Française, GEPASUD, Tahiti.
³Harvard University, Cambridge, 02138 MA, USA.

Understanding mechanisms that modify landscapes is essential for risk assessment in tropical islands. Such an understanding requires quantification of the rates at which landscapes respond to tectonic and climatic signals. Because measurements of long-term erosion rates are critical for understanding landform evolution, the use of cosmogenic isotopes in river sediments to estimate average erosion rates of drainage areas has grown rapidly in recent years.

In this study we present measurements of cosmogenic ³He concentrations ([³He]) in olivine grains from Tahitian river sediments (French Society Island) to predict the spatial pattern of erosion rates in the drainage area [1].

The olivine-rich sands come from 3 locations along the Matatia River, on the west part of Tahiti (catchment mouth, intermediate and upstream positions). He concentrations and isotopic ratios have been measured in 3 samples of olivine grains (1-2 mm) each weighing ~500 mg. The [³He] has been calculated using: (i) the ³He/⁴He ratio measured by crushing and (ii) the ³He and ⁴He concentrations measured by melting the resulting powder.

Initial results indicate (i) an average erosion rate of 0.39±0.19 mm/yr upstream of the catchment mouth, and (ii) an average erosion rate of 0.0078±0.0007 mm/yr for the upstream sub-basin. The erosion rate at the intermediate position is too high to accumulate measurable amounts of ³He.

The observed variation of erosion rates along the drainage area could be related to different erosional processes (landslides vs. soil creep), or can represent the erosion rates of different sub-basins (main stream vs. tributary). The measured erosion rates at the different locations allow us to invert for the spatial distribution of the erosion rates through nonlinear slope- and curvature-dependent erosion rates. This approach also enables us to constraint the form of parameterized erosion laws.


Melting conditions with PRIMELT: Examples and future work

ESTEBAN GAZEL¹, CLAUDE HERZBERG² AND PAUL ASIMOW³

¹Lamont-Doherty Earth Observatory, (egazel@ldeo.columbia.edu)
²Rutgers University, (herzberg@rci.rutgers.edu)
³California Institute of Technology, (asimow@gps.caltech.edu)

Determination of the magmatic melting conditions in the mantle is important for understanding the origin of intraplate magmas. The major element composition of primary magmas can provide such information, but there are important limitations. Of these, the best known is fractional crystallization. Other factors are source lithology variations and volatile content. PRIMELT2 [1] was introduced to calculate primary magma composition, but is restricted to primitive lavas that only crystallized olivine. It was calibrated from experiments on fertile mantle peridotite, and provides a mass balance primary magma. It calculates primary magma composition, melt fraction for accumulated fractional and batch melting, mantle potential temperature, olivine phenocryst composition, and warns the user of potentially compromising effects of source lithology variations and CO₂ content.

PRIMELT2 was used to evaluated variations in mantle potential temperature of OIB (ocean islands) [1] and to compare OIB to Large Igneous Provinces (LIPS) [2]. Results show that mantle plumes for LIPS were hotter and melted more extensively than plumes of modern OIB. Petrological solutions obtained from back-arc alkaline lavas from the Central American Volcanic Front yield Tₚ estimates within expected ambient mantle (1350-1400°C) [3]. These results indicate that PRIMELT2 is applicable for melting in a variety of tectonic environments. Work in progress will test the effects of alteration and simulate a decompression melting path.

How geochemical proxies provide quantifiable evidence of climate shifts over the last 25,000 years

GEOFFREY GEBBIE
Department of Physical Oceanography, Woods Hole Oceanographic Institution, MS #29, Woods Hole, MA 02543 USA (ggebbie@whoi.edu)

Some of the best, but still limited, evidence for large climate shifts, including the end of the Last Ice Age, comes in the form of geochemical proxies preserved in seafloor sediments. The proxy data is actually recording oceanic tracer distributions, which in turn, depend upon the sea surface and the atmosphere in a complicated way. In the terminology of inverse methods, the “observation step” must be modelled as well; that is, the process that translates the physical variables of the ocean into a proxy signal must be explicitly (i.e., mathematically) stated. In many cases, this process is calcification in foraminifera, and empirical relationships are used here as the model of this step. In cases where the observation or proxy step is oversimplified in the model, a whole range of plausible solutions can be excluded without good reason.

While it is clearly of interest to estimate past rates of ocean circulation from geochemical proxies, an inverse method is used to show that the seafloor proxies from the Last Glacial Maximum inform us primarily about shifts in the water-mass configuration. In this particular example, I show that the geochemical proxies, δ18O, δ13C, and Cd/Ca ratio, give quantifiable evidence for a shift in the pathways of the interior ocean, not just changes in surface boundary conditions. Given this information, estimates of the rate of overturning circulation in the Atlantic are revisited, but significant uncertainties remain in the inverse estimate of this particular quantity.

Selenium reduction by pyrite: pH effect and Mossbauer study

ANTOINE GEHIN1, MINGLIANG KANG1,2, JEAN-MARC GRENECHE3 AND LAURENT CHARLET1
1Environmental Geochemistry Group, ISTerre, Maison des Geoscience, 38041 Grenoble, France
(*correspondence: antoine.gehin@obs.ujf-grenoble.fr)
2Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, P.R. China
3Condensed Matter Physics Laboratory, IRIM2F, University of Maine, 72085 Le Mans, France

The radioactive isotope 79Se is presently considered as the key mobile fission product for the disposal of spent fuel (SF) and high-level radioactive waste (HLW). Its solubility is largely controlled by oxidation state. Due to the weak adsorption of Se(IV) and Se(VI) on natural minerals, especially on granite and clay minerals, chemical reduction is considered to be the most effective way to immobilize 79Se [1,2].

On the other hand, pyrite is the most frequent sulfide mineral and is also present in geological barriers of nuclear waste repositories [3].

Therefore, we investigate the interaction between pyrite and Se(IV) from pH 5.05 to 8.5. After 1 month, solution analyses show that Se(IV) concentration decreases under the detection limit and suggest that Se(IV) is involved in redox reactions with FeS2.

We focus specially on the behavior of iron species in the immobilization of Selenium. Mossbauer spectroscopy performed on the solid at different pH shows clearly significant iron environment modifications, and thus it suggests particularly the precipitation of new solid phases included Fe and Se, like FeSe or FeSe2.

These results are confirmed by XAFS spectroscopy used to unravel the selenium speciation, and microscopy analysis (SEM and TEM).

U-Pb ages and Hf isotopes of detrital zircons from miogeoclinal strata of western North America

GEORGE GEHRELS AND MARK Pecha
Department of Geosciences, University of Arizona, Tucson AZ 85721 USA (ggehrels@gmail.com)

U-Pb ages and Hf isotope signatures have been determined from 32 samples of Neoproterozoic, Paleozoic, and lower Mesozoic miogeoclinal strata from western North America. Samples have been collected along five transects in eastern Alaska, northern British Columbia, southern British Columbia, Utah-Nevada, and northern Mexico. Detrital zircon grains from these samples were analyzed for U-Pb by ID-TIMS in the mid-90’s to generate a spatial-temporal reference for the ages of grains that accumulated along the western edge of North America. We have recently re-analyzed these samples by CL-based LA-MC-ICPMS to determine more robust U-Pb age distributions (~200 grains/sample) as well as complementary Hf isotope signatures (~50 grains/sample).

U-Pb ages from these samples match well with the ages determined by ID-TIMS, and in most cases resemble the ages of nearby basement rocks. Hf isotope signatures for these detrital grains reveal a fascinating history of crustal genesis and recycling. In southern regions, primary age groups are 1.0-1.2, ~1.4, and 1.6-1.8 Ga, which matches the ages of bedrock terranes in the region. Hf signatures of these grains record generation of juvenile crust at 1.6-1.8 Ga, followed by recycling of this crust during younger magmatism. Central transects contain these same age groups, plus a significant Late Archean contribution. Hf data suggest formation of juvenile crust during Late Archean time, with significant recycling of this crust during 1.6-2.2 Ga magmatism. Little juvenile crust is recorded between 1.6 and 1.8 Ga, whereas, surprisingly, 1.0-1.2 and ~1.4 Ga zircons are considerably more juvenile than coeval grains to the south. Northern transects record protracted magmatism from 3.6 Ga to 300 Ma. Some juvenile crust of early Paleozoic, Early Proterozoic, and Late Archean age is represented, but most grains have Hf compositions that lie between observed 1.8-2.0 and 2.5-2.8 Ga evolution bands. This presumably reflects homogeneous mixing of 1.8-2.0 and 2.5-2.8 Ga crust, rather than recycling of 2.0-2.3 Ga juvenile crust, as the 2.0-2.3 Ga grains present are not juvenile.

Actinium-227 in the Atlantic sector of the Southern Ocean: New results from Bonus-Goodhope and UK Geotraces

WALTER GEIBERT1*, ALAN HSIEH2, CLAUDIA HANFLAND3, ELISABET VERDENY4, PERE MASQUE4, GIDEON HENDERSON7

1School of GeoSciences, University of Edinburgh, West Mains Road, Edinburgh EH9 3JW, UK
(*correspondence: walter.geibert@ed.ac.uk)
2Department of Earth Sciences, University of Oxford, UK
3Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany
4Institut de Ciència i Tecnologia Ambientals - Departament de Física, Universitat Autònoma de Barcelona, Spain

Actinium-227 is a naturally occurring radionuclide, which is released from marine sediments, in particular deep-sea sediments. With a half-life of 21.77 years, it is an excellent indicator of vertical mixing in the deep-sea, and a tracer for upwelling of deep water masses. Therefore, it has potential to be used to quantify fluxes of micronutrients from the deep-sea.

Here, we present new data from the Southern Ocean that were obtained during the UK Geotraces cruise and the Bonus-Goodhope cruise in the South Atlantic. We characterise the main water masses in the Atlantic sector of the Southern Ocean, and discuss to which extent the Ac data can be expected to remain constant over time within water masses. We also compare results that were obtained by direct alphaspectrometric analyses (Bonus-Goodhope) to indirect measurements by radium delayed coincidence counting (RaDeCC) and discuss the differences of the methods.

If a general input function for Ac from marine sediments could developed, 227Ac could be used to validate deep ocean circulation and mixing in models, analogue to the application of 3H or chlorofluorocarbon as tracers for surface water masses. New depth profiles from the UK Geotraces cruise promise to give new estimates of 227Ac flux from the deep sea, and bring the implementation of 227Ac in models closer.
Si-isotope fractionation during silica precipitation: An experimental approach

S. GEILERT1*, M.J. VAN BERGEN1 and P.Z. VROON2
1Department of Earth Science, Utrecht University, the Netherlands (*correspondence: geilert@geo.uu.nl)
2Faculty of Earth and Life Sciences, Vrije Universiteit Amsterdam, the Netherlands

Interpretations of silicon isotope compositions of natural silica deposits suffer from poor constraints on the isotopic fractionation behaviour during precipitation of the silica from a saturated solution. We tested an experimental setup to explore the conditions under which equilibrium precipitation of amorphous silica would occur in the 10-60°C temperature range using flow-through reactors. The objective is to constrain magnitudes and sign of silicon isotope fractionation, the degree of temperature dependence and the sensitivity to non-equilibrium conditions.

Stock solutions, prepared from amorphous silica powder and brought to saturation at 90°C, were forced to pass flow-through reactors, seeded with ca. 200 mg of silica powder with known surface area at well-controlled flow-rates. Precipitation was induced by placing the reactors in a water-bath at the desired temperature. According to a comprehensive set of test runs, our experimental set-up enables us to achieve equilibrium during controlled silica precipitation in the reactors, provided that conditions are carefully tuned. Factors with a strong influence included the applied flow-rate, pH, specific surface area and degree of supersaturation.

Silicon isotope measurements (30Si/28Si and 29Si/28Si), carried out on input and output solutions using a Finnigan Neptune MC-ICPMS, presented insight into the sign and magnitude of isotopic fractionation. Preliminary results for runs where equilibrium was secured demonstrated that, under these experimental conditions, δ30Si values for SiO2 remaining in solution were up to 0.5‰ lower relative to the input solution, implying discrimination against the uptake of the lighter isotopes in the solid. The fractionation increased with decreasing temperature.

The observed direction is opposite to what is often seen in natural solid-fluid systems, indicating that equilibrium versus non-equilibrium conditions during precipitation might be a critical factor in the use of Si isotopes as a proxy.

The rusty sink: Impact of Iron on the sedimentary organic biomarker record

YVES GÉLINAS1*, KARINE LALONDE1, LUC TREMBLAY2, ANJA MORITZ1 and ANDREW BARBER1
1Chemistry and Biochemistry, Concordia Univ., Montreal (QC), Canada, H4B 1R6 (*correspondence: ygelinas@alcor.concordia.ca)
2Chimie et Biochimie, Univ. Moncton, Moncton (NB), Canada, E1A 3E9 (luc.tremblay@umoncton.ca)

The biogeochemical cycles of iron (Fe) and organic carbon (OC) are strongly linked, each element exerting some degree of control over the other. In the oceans, organic ligands control the concentration of dissolved Fe in the water column. In soils, Fe and OC concentrations are typically correlated, suggesting that they are closely associated. Nevertheless, until now, the role of Fe in the preservation of sedimentary OC has not been clearly established. We recently determined that 20 to 40% of the total OC in marine and freshwater sediments is closely associated to solid reactive Fe phases (operationally defined as the solid iron phases that are reductively dissolved with sodium dithionite). In young and mature sediments, solid reactive Fe phases do not provide sufficient surface area for chemisorption of OC onto Fe oxides. Alternatively, high OC:Fe ratios reflect the existence of largely organic Fe–OC macromolecular structures (through chelation and co-precipitation), attached only minimally to the surface of clay mineral grains. The organic matter in these Fe–OM chelates is ‘glued’ together by iron ions or nanophases of iron oxide crystals. We also found isotopic and elemental fractionation between Fe–associated OC and the rest of the sedimentary OC pool, with 13C and nitrogen-enriched OC preferentially bound to Fe, and suggesting biochemical fractionation. The presence of iron and the interactions between iron and organic matter also affect the recovery of a broad range of organic biomarkers from sediments. In this communication, we will present and discuss the impact of iron on the recovery of amino, lipid and lignin biomarkers as well as on the environmental message obtained through biomarker analysis. Alternative methods that circumvent the effects will also be presented.
T and fO2 guided, gas phase mediated Na and K exchange between silicate melt drops

M. Gellissen1,2, A. Holzheid1, Ph. Ke格尔1 and H. Palme2

1Univ. Kiel, Inst. f. Geowissenschaften; (mgellissen@web.de)
2Forschungsinstitut und Naturmuseum Senckenberg, Frankfurt a.M.

The overall depletion of volatile lithophile elements in the mantles of the terrestrial planets along with nearly unfractionated Mn/Na ratios [1] as well as the varying abundances of Na and K relative to Si in meteorites and even individual chondrules [2] leads to the question of the nature of the depletion process (evaporation or incomplete condensation). As our early experiments showed little or no loss from Na and K bearing minerals we focussed on evaporation from siliceous melts with different fractions of Al, Na, K and partly Fe, Ti and Mn.

We used 11 synthetic silicates with a molar Si/(Al+Na+K) ratio of 3/1, varying Al/alkali and Na/K ratios and NBO/T from 0 to 0.67. Each run contained samples of different composition. Also a Si, Fe, Ti and Mn bearing mixture enriched with Na and K was used. Samples’ weights were about 4 mg. Time series were done in 1 atm CO/CO2 gas mixing furnaces from 1000 to 1550 °C and log fO2 from air to IW-2. Sample mounting was by Pt wire loop technique [3].

Under all experimental conditions Na and K are lost from high Na, K samples and gained by low Na, K samples, with all samples reaching an approximately constant level after several hours. The process is faster with increasing temperature and decreasing oxygen fugacity. The Na concentration at the converging point decreases with increasing gas flux, but is independent of Al concentration in the starting composition, despite variations from 0 to 26 wt % Al2O3. The effect for K is less pronounced.

Na and K contents are controlled by the Na and K vapor pressures in the furnace, which again is determined mainly by the gas flow in the furnace and by the total amount of alkalis released by heating. The lesser dependence of the K concentration from the gas flux is a hint to a faster kinetic behavior compared to the Na. More experiments with varying gas flow rates are in progress.


Petrology of the Middle Eocene sub-volcanic association of Western Pontides

S. Can Genç1, Fatma Gülmez1, Mehmet Keskin2, Okan Tüysüz2 and Turgay İşseven4

1ITU Dept of Geology 34469 Istanbul, Turkey
2IU Dept. of Geology Istanbul, Turkey;
3ITU Inst. of Eurasian Earth Sci., 34469 Istanbul, Turkey;
4ITU Dept. of Geophysics 34469 Istanbul, Turkey;

The Middle Eocene (49.3±2 – 38.1±1.9 Ma) magmatic rocks (MEMR) form an east-west trending belt along the northern Turkey. They rest unconformably on the pre-Middle Eocene units. Here, we present geological and petrological data from the western part of this belt, between Armutlu Peninsula and the Almack Mountains. These rocks forming a “sub-volcanic association” are represented by the basic to intermediate volcanic rocks, dikes and coeval granitic rocks. The volcanic rocks of the MEMR form a continuous trend from basalt to dacite. Granitic rocks comprise granite, granodiorite and tonalities. Both the volcanic and the granitic rocks display medium-K subalkaline affinity, and CA trend with rare tholeiitic lava samples. They display significant enrichment in LIL elements, and slightly enrichment in LREE. There are apparent impoverishments in Ta and N, in N-MORB normalized spider diagrams. Initial Sr and Nd isotopic values for the volcanic rocks of the MEMR are (⁸⁷Sr/⁸⁶Sr): 0.703976-0.706441 and (¹⁴⁷Nd/¹⁴⁴Nd): 0.512856-0.512601), respectively. From these data and combined ENd(T) (-1.55 - +5.38), Pb and ¹⁸O (8.5-13) isotopic values, we conclude that the magma produced the MEMR was hybrid in composition, including depleted mantle and crustal components. AFC processes played an important role for the genesis of magma. According to these geochemical features, MEMR displays close similarity to the subduction-related magmas. In the light of geological and petrological findings, we conclude that the MEMR was produced in a post-collisional setting, and we favour the slab breakoff model that provides a better explanation for the generation of the MEMR.
Redox reactions of Fe$_{II}$-III oxyhydroxycarbonate minerals in gleysols, fougérite, trébeurdenite and mössbauerite, and water denitrification

J.-M. R. GENIN$^{1, *}$, O. GUÉRIN$^{2}$, E. KUZMANN$^{3}$ and C. RUBY$^{1}$

$^1$Institut Jean Barriol, Université Henri Poincaré, ESSTIN, 2 rue J. Lamour, F54500, Vandoeuvre-lès-Nancy, France
($^*$correspondence: jean-marie.genin@esstin.uhp-nancy.fr)

$^2$Laboratoire de Géomorphologie, Ecole Pratique des Hautes Etudes, 15 bd de la mer, F35800, Dinard, France

$^3$Department of Chemistry, Eötvös Lorand University, Pazmany Peter setany, H1117, Budapest, Hungary

Colour change from bluish-green to ochre in gleysols is due to redox reactions within Fe$_{II}$-III oxyhydroxycarbonate, related to a green rust Fe$_{II}$-III double layered hydroxide of general formula Fe$_{6(1-x)}$Fe$_{3x}$ (OH)$_{2(7-3x)}$O$_3$CO$_3$•3H$_2$O. Minerals are named (i) fougérite for Fe$_{4}$Fe$_{2}$ (OH)$_{12}$ CO$_3$•3H$_2$O green rust Fe$_{II}$-III hydroxycarbonate (ii) trébeurdenite for Fe$_{II}$_2 Fe$_{III}$_4 (OH)$_{10}$O$_2$CO$_3$•3H$_2$O Fe$_{II}$-III oxyhydroxy-carbonate (iii) mössbauerite for Fe$_{III}$_6 (OH)$_8$O$_4$CO$_3$•3H$_2$O ferric oxyhydroxycarbonate at definite $x$ values of 0.33, 0.67 and 1, respectively; the exceptional redox flexibility comes from toptotactic reactions as shown by XRD and TEM; the relative trivalent cation average ratio $x$ extends from 0.33 to 1 by mixing minerals as shown by Mössbauer spectra (Fig. 1).

Figure not supplied.

Figure 1: Mössbauer spectra measured at 78 K of samples vs $x$ (a) fougérite; (b) trébeurdenite (c) mössbauerite

In samples extracted out of waterlogged gleys in a water table (Fougères), $x$ varies between 0.33 and 0.67 by mixing fougérite with trébeurdenite, whereas in those extracted from the schoror of a maritime marsh (Trébeuren), $x$ varies between 0.67 and 1 by mixing trébeurdenite and mössbauerite, due to partial oxidation of the gleys at low tide. This redox flexibility is responsible for water denitrification in water tables combined with anaerobic bacterial reduction.

Plume-ridge interaction:
Constraints on melting dynamics from the Azores and Iceland

F.S. GENKSE$^{1, 2, *}$, C. BEIER$^{1, 2}$, S.P. TURNER$^1$, K.M. HAASE$^2$ and B.F. SCHAEFER$^1$

$^1$GEMOC, Department of Earth and Planetary Sciences, Macquarie University, Sydney NSW 2109, Australia
($^{*}$correspondence: felix.genske@mq.edu.au)

$^2$GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Schloßgarten 5, D-91054 Erlangen, Germany

Ocean Island Basalts (OIB) erupted in the vicinity of Mid-Ocean Ridges (MOR) provide important information on melting processes, melt movement and composition of the Earth’s mantle. In particular the major element, trace element and Sr-Nd-Pb isotope ratios allow for constraints on the distinct melting behaviour of enriched and depleted mantle sources, their along and across axis distribution and potential changes in melting depth and melting temperatures.

While the flow of melts into the Mid-Atlantic Ridge (MAR) in the Azores and Iceland has been the subject of several studies, both plumes exhibit active volcanism on the western side of the Mid-Atlantic Ridge away from the proposed plume locality. Such off-axis volcanism beneath the North-American plate is comparable for the two OIB settings in terms of trace element and isotopic source composition relative to the main plume centre. Incompatible trace element ratios of Nb/Zr, Ta/Hf and La/Sm are elevated by similar factors in the off-axis (western) lavas when compared to the lavas from the plume centre. We compare the melting dynamics (i.e. P-T conditions of basalt generation) underneath the Snaefellsness peninsula (Iceland) with those underneath Flores and Corvo islands (Azores); both examples of unusual off-axis and “off-plume” magmatism.

We demonstrate that Iceland and the Azores exhibit comparable excess temperatures, but that melting underneath the western Azores islands is initiated deeper. The sources in the Azores are more enriched and degrees of partial melting are slightly lower than compared to Snaefellsness. This implies that for both cases melting dynamics are largely controlled by the geochemochemical composition of the source and possibly lithosphere thickness rather than upwelling rate. The differences between eastern and western (i.e. plume related vs. "off-plume") sources may reflect different proportions of enriched melts during binary mixing with depleted MORB mantle (DMM) sources.
Weathering of black shales and Re-Os isotope systematics

S. GEORGIEV1,2*, H. STEIN2,1, J. HANNAH2,1, B. BINGEN1,2, V. HATLØ3, E. REIN3, S. PIASECKI4, H. WEISS5 AND G. XU2,1

1Geological Survey of Norway, 7491 Trondheim, Norway
2AIRIE Program, Colorado State University, USA
(*correspondence: georgiev@colostate.edu)
3Statoil ASA, 5254 Sandsli, Norway
4Geological Survey of Denmark and Greenland (GEUS)
5SINTEF Petroleum Research, 7465 Trondheim, Norway

Late Permian organic-rich shales from the Ravnefjeld Fm in East Greenland yield a precise isochron from drill core samples, but scattered data from outcrop samples. Using Re-Os isochroneity as a gauge to distinguish fresh undisturbed shale from macroscopically fresh but chemically altered shale, we explore additional geochemical parameters that evidence subtle weathering and oxidation of shale.

Systematic differences between weathered and fresh samples are used to characterize and quantify the effect of weathering on shale chemistry. Weathering oxidizes organic matter (OM) and sulfides (mainly pyrite framboids < 6 µm on average), sometimes imperceptibly. The kerogen oxygen content (approximated by the S3 parameter of Rock-Eval pyrolysis) is a more consistent proxy for weathering than major or trace element compositions. Comparison with time equivalent fresh shale from the mid-Norwegian shelf reveals that shale weathering is best detected and characterized by the combined use of Rock-Eval indices for oxidation of OM and sulfur content data that document oxidation of pyrite. Based on this example, we present a sampling strategy to optimize the potential for accurate and precise Re-Os geochronology.

Correlations among trace metals, total organic carbon and total sulfur show that both Re and Os are concentrated in OM rather than sulfides. While both Re and Os are mobile during weathering, isotopic disturbance may occur through several contrasting mechanisms depending on local factors from the outcrop to the mm-scale. Depending on the type of isotopic disturbance, weathered shales may yield erroneously younger or erroneously older model ages.

Late Permian shales in this study have exceptionally high Re/Os ratios that lead to rapidly increasing $^{187}$Os/$^{188}$Os with time. Mass balance shows that recent (or Cenozoic) weathering of such shales may influence the Os isotopic composition of seawater much more strongly than weathering of typical Phanerozoic shales; the effect will be comparable to weathering of Precambrian shales.

Funded by Norwegian Research Council Award 180015/S30.

Modeling the effects of fertilization and pH on dissolved inorganic phosphorus in soils

F. GERARD1, N. DEVAU1, E. LE CADRE2 AND P. HINSINGER1

1INRA, UMR 1222 Eco&Sols, Montpellier, France
2Supagro, UMR 1222 Eco&Sols, Montpellier, France

We used a set of mechanistic (macro-scale) adsorption models within the framework of the component additive approach in an attempt to determine the effect of repeated massive application of inorganic P fertilizer on the processes controlling the concentration of dissolved inorganic phosphorus (DIP) in soils. We studied a Luvisol with markedly different total concentrations of inorganic P as the result of different P fertilizer history (i.e. massive or no application for 40 years). Soil pH was made to vary from acid to alkaline.

Satisfactory results were obtained using generic values for model parameters and soil-specific ones, which were either determined directly by measurements or estimated from the literature. We showed that adsorption largely controlled the variations of DIP concentration and that, because of kinetic constraints, minor precipitation of Ca-phosphates may have occurred under alkaline conditions, particularly in the P-fertilized treatment. The adsorption of Ca$^{2+}$ onto soil minerals promoted adsorption of phosphates through electrostatic interactions. The intensity of this mechanism was high under neutral to alkaline conditions. The variation in DIP concentration with pH can be related to changes in the contribution of the various soil minerals to P adsorption.
Advances in analyses of radiogenic isotope by LA-MC-ICPMS:
The importance of mass bias and interference correction

A. GERDES
Institut für Geowissenschaften, Goethe University Frankfurt, Altenhoeferallee 1, D-60438 Frankfurt am Main (gerdes@em.uni-frankfurt.de)

Isotope analysis by laser ablation sector-field ICP mass spectrometry (LA-SF-ICPMS) becomes increasingly important to study magmatic, metamorphic, and sedimentary processes. The information gained can be, for instance, crucial for a better understanding of the timing and genesis of magmatic and sedimentary rocks, the formation of ore deposits, and the evolution of the continental crust. Due to disturbance of the isotope system by alteration and partial recrystallization the initial isotope composition is often preserved only in single growth domains of minerals.

Developments in LA-SF-ICPMS over the last years make it now possible to analysis precisely the isotopic composition of Sr, Nd, Hf, and U-Th-Pb with a spatial resolution of down to 30 to 5µm, depending on elemental concentration. Hence, a very sensitive detection system coupled to powerful Laser with short wave length and high resolution imaging system is crucial for this type of analyses.

Besides high background (e.g., gas blank), matrix effects, and mass bias correction, the precision and accuracy of these isotope analyses often strongly suffers from isobaric and molecular interferences on the relevant masses. Although these interferences in question can be usually monitored simultaneously on a different mass, the interference correction is hampered by prediction of the mass discrimination behaviour of this isotope pair.

Data will be shown that the discrimination of the lighter isotopes in the plasma interface of the ICP-MS is dependent on element and on the matrix. With examples from the different isotope system, analytical protocols will be discussed to overcome this problem. The results of recent studies performed in our lab demonstrate that LA-MC-ICPMS analyses of $^{87}$Sr/$^{86}$Sr (e.g., plagioclase, titanite, apatite, monazite, xenotime, pyrochlore, perovskite), $^{143}$Nd/$^{144}$Nd (e.g., titanite, monazite, apatite, pyrochlore, perovskite, garnet) and $^{187}$Hf/$^{188}$Hf (e.g., zircon, zirconolite, baddeleyite) isotopes can be precise and accurate to about 0.01% or better, despite of 10 to >50% interference on the relevant isotope ratio. Providing that between different phases the range in the mother-daughter isotope ratio is sufficient large enough, it is even possible to obtain geologically meaningful isochrones in the Rb-Sr and Sm-Nd system by LA-MC-ICPMS analyses.

Geochemical signatures of thermochemical sulfate reduction – Ketones and sulphur species

S. GERMEROTT1, C. OSTERTAG-HENNING2 AND H. BEHRENS1
1Institute for Mineralogy, Leibniz University of Hannover, Callinstr. 3, 30167 Hannover, Germany (*correspondence: s.germerott@mineralogie.uni-hannover.de)
2Federal Institute for Geosciences and Natural Resources, Stilleweg 2, 30655 Hannover, Germany

Thermochemical sulfate reduction (TSR) is defined as the abiological, thermally-driven reduction of sulfate with H$_2$S and CO$_2$ as major reaction products. The reaction can proceed at temperatures above 120°C when sulfate as well as reducing agents, such as e.g. hydrocarbons or ferrous iron, are present. In spite of its great importance for hydrocarbon reservoir alteration and sulfide ore formation, the TSR process is not adequately understood. In this study we present findings from laboratory experiments that lead to an improved description of the geochemical signature of TSR and thus to a better understanding of TSR reaction mechanisms. A major goal was to identify key chemical compounds that play an important role during TSR.

Experiments were performed in sealed gold capsules, at 300°C and 350°C, 350 bar, for a duration of 24 - 336 h. A redox-mineral buffer, consisting of pyrite (FeS$_2$), pyrrhotite (Fe$_3$S$_4$) and magnetite (Fe$_3$O$_4$) was used to constrain the redox conditions during the experiments. Na$_2$SO$_4$, dissolved in water, was used as sulphate source and C$_8$H$_{18}$ as model hydrocarbon (= reducing agent). Furthermore, the influence of elemental sulphur on the TSR reaction was investigated. After the experiments the products were analyzed by different gas chromatographic techniques. In addition to CO$_2$ and hydrocarbons, we focused on the analysis of ketones and organosulphur compounds.

In general, a higher reaction rate was found at 350°C compared to 300°C. Concurrent processes in the degradation of octane under the experimental P-T conditions comprise cracking and TSR reactions. A pronounced influence of TSR was indicated by the formation of CO$_2$, ketones, aromatics and organosulphur compounds. The experiments with elemental sulphur showed the highest yields of TSR products. The analytical data suggest that the oxidation of carbon proceeds via one or more intermediate reaction steps with metastable oxygenated or sulfurized compounds, e.g. the formation of ketones.
Subcrustal CO₂ flux measurement in the Hranice hydrothermal Karst

MILAN GERŠL¹*, EVA GERŠLOVÁ¹, DUŠAN HYPR² AND VLADIMÍR KOLEJKA³

¹Czech Geological Survey, Brno branch, Leitnerova 22, 679 36 Brno (*correspondence: milan.gersl@geology.cz)
²Czech Speleological Society, 6-18 tartaros, Brno

In the Hranice Karst (Czech Republic) the term thermomineral karst was introduced to the international literature [1]. This active thermal karst is developed in the sequence of Paleozoic limestones as a result of deep influx of thermal water charged with subcrustal carbon dioxide (CO₂). Gas origin is also supported by helium isotopic ratio in water-gas mixture [2]. The carbon dioxide concentration in Zbrašov aragonite cave atmosphere reflects seasonal temperature variation and is well documented and described for the last 30 years [3].

Measurement techniques

CO₂ flux measurement was performed in 2009–2010 using accumulation chamber equipped with infrared analyzer in the Hranice field area. CO₂ flux was measured in the Zbrašov aragonite cave system during the summer 2010. The cave atmosphere was suck out to get permanent flow of CO₂. This status was hold for 6:27 hours. Chemical and isotopic composition of selected gas samples were determined in the laboratory by gas chromatography / mass spectrometry.

The average CO₂ concentration was 2.529% and flux ranged from 74 to 125 g.m⁻².d⁻¹ reflecting venting of subcrustal CO₂ in the Hranice area. In the Zbrašov aragonite cave the CO₂ concentration in the atmosphere varies from 0 to 85% with measured constant flux of 32894.45 g.m⁻².d⁻¹.


Ophiolites of the Kuznetzky Alatau Ridge (SW Siberia) as a possible ancient crust fragments of the Paleoasian Ocean

I.F. GERTNER* AND T.S. KRASNOVA

Tomsk State University, Lenin avenue 36, 634050 Tomsk, Russia, (*correspondence: labspm@ggf.tsu.ru)

An assessment of initial stages of the Paleoasian Ocean opening is still a matter of researcher’s argument. Besides it assumes a quite long time interval which, according to the geodynamic reconstructions within Altay-Sayan folded area, ranging from 700 to 1000 Ma. One of the reasons for doubts about geochronology evaluation of the ophiolitic suite fragments is isotopic data absence for the rocks with ultrabasic and basic composition which are oceanic crust and lithospheric mantle standard.

Ophiolites of the Kuznetsky Alatau Ridge trace an ancient suture zone formed as a result of the collision of few arc island terrains on the active margin of Siberian continent during the Late Cambrian and Early Ordovician time (530-480 Ma). Their absolute ages was recently estimated by the Sm-Nd mineral isochron for the amphibolite (694±43 Ma) and results of U-Pb dating of zircons from the plagioriolite spaitly associated with ocean basalts (544±8 Ma). According to regional geological conclusions the real temporal range of ophiolite forming is about 500 Ma (from Early Cambrian to Late Riphean time). Our data of Sm and Nd isotopes for the whole rocks of mantle hyperbasites and ultramafic-mafic rocks are close to ancient boundary of these rocks.

The Sm-Nd isochron based on the three whole rock samples of harzburgite, chromitite and dunite has a slope corresponding to the age 947±51 Ma at MSWD = 1.18. But the 6-point regression line based on the whole rocks magmatic peridotites and gabbroids of toleitic series is a more reliable. Its slope corresponds to the age 943±39 Ma at MSWD = 0.966. In particular the restitic ultrabasites correspond to the characteristics of the strongly depleted backarc basin -type mantle substrate. Their model age calculation with using modern depleted mantle model certainly suggests a younger initial substrate. For the “restitic” ultrabasites T (DM) values range from 760 to 866 Ma, whereas for “magmatic” rocks these values corresponds to the real isochron age of 945-1000 Ma. These data confirm a possible geochemical heterogeneity of ultramafic-mafic complexes in the suture zone of the thrust-folded systems.

The study was funded by Russian Ministry of Education and Science.
Mantle heterogeneities beneath Laguna Timone volcano, Pali Aike volcanic field, Southern Chile

F. GERVASONI1*, R.V. CONCEIÇÃO1, T.L.R. JALOWITZKI1 AND Y. ORIHASHI2

1Geoscience Institute, UFRGS, Porto Alegre - RS, Brazil
(*correspondence: fernanda.gervasoni@ufrgs.br)
2Earthquake Research Institute, The University of Tokyo, Tokyo, Japan (oripachi@eri.u-tokyo.ac.jp)

Laguna Timone (52°01′39″S, 70°12′53″W), inactive Quaternary volcano in Pali Aike volcanic field [1], southern Chile, host large mantle xenoliths from the lithosphere. They are characterized by spinel-lherzolite, garnet-spinel-lherzolite, garnet-harzburgite, glimmerite (PM18-3) and some xenoliths are phlogopite- and/or pargasite-bearing, which suggest their origin in mantle deeper source and a metasomatism. Geochemical data show #Mg between 88 to 91 and major elements depletion compared to primitive mantle (PM) [2]. Rare earth elements (REE), normalized to PM, suggests four: Group 1 has light REE depletion and heavy REE enrichment (CeN/YbN= 0.12-0.43); Group 2 has LREE enrichment and HREE depletion (CeN/YbN=2.07-15.3); Group 3 have middle REE enrichment and depletion (CeN/YbN= 0.96-0.98), and Group 4 have similar values between LREE and HREE (CeN/YbN= 0.78-1.68). All samples are more enriched in Ta than Nb, and are strongly depleted in Y; Zr and Hf are enriched in most samples. The Sr and Rb are depleted while Ba is enriched. Spider diagrams show anomalies in some samples such as Nb, Ta, Zr and Hf high enrichment in sample PM18-3. Calculations with no-modal batch melting model shows that Laguna Timone xenoliths have suffered ~20% of melt. The Rb-Sr, Sm-Nd and Pb-Pb isotopes analysis are under progress. Laguna Timone xenoliths came from a deep source in the Patagonian mantle and suffered several thermal multi-stage, indicated by mineralogic evidence (garnet-lherzolite to spinel-lherzolite transitions phases) and a modal metasomatism (phlogopite and pargasite).


---

Geodynamic regimes of continental crust growth and lithosphere reworking in subduction zones

TARAS GERYA

Institute of Geophysics, Swiss Federal Institute of Technology, Sonneggstrasse 5, 8092 Zurich, Switzerland, (taras.gerya@erdw.ethz.ch)

It is widely accepted that new continental crust can grow in subduction zones. Indeed, physical-chemical controls and dynamics of crustal addition remain partly enigmatic. Based on numerical models we identify the following geodynamic regimes of subduction, crustal growth and lithospheric reworking which may potentially form on Earth: (1) stable subduction, (2) retreating subduction with a focused backarc spreading center, (3) retreating subduction with distributed intra-arc extension, (4) advancing subduction with thickening overriding plate. Transitions between these different regimes are mainly caused by the concurrence of rheological weakening effects of (1) aqueous fluids percolating from the subducting slab into the mantle wedge and (2) melts propagating from the partially molten areas formed in the mantle wedge toward the surface. The aqueous fluids mainly affect the forearc region. Strong fluid-related weakening promotes plate decoupling and reduces subduction drag and thus results in stacking of sediments in the accretion prism. In contrast, reduced weakening by fluids results in strong coupling of the plates and leads to advancing collision-like subduction with enhanced subduction erosion. Thickening of the overriding plate and sedimentary plumes in the mantle wedge are the consequences. On the other hand, melts, extracted from the hot regions above the slab, rheologically weaken the lithosphere below the arc which thus controls overriding plate extension and shortening. Strong rheological weakening by melts in combination with weak plate coupling triggers retreating subduction with a pronounced backarc spreading center. Also, weakening of the arc by melts extracted from sedimentary plumes, generate weak channels through which these structures may be emplaced into subarc crust. If there is insufficient melt-related weakening, plumes cannot ascend but extend horizontally and thus underplate the lithosphere. Models with notable melt- and fluid-related weakening often predict existence of hot, rheologically weak asthenospheric window in the bottom of the arc that allows for potential relamination of positively buoyant subducted rocks to the crust and recycling of dense magmatic residue back into the mantle.

Mineralogical Magazine www.minersoc.org
Time constraint on Brunhes-Matuyama inversion inferred by U-Series disequilibrium

B. GHALEB1, C. FALGUÈRES2, J.P. POZZI2, L. ROUSSEAU2, J. CARLUT3 and L. BOUDAD 5

1GEOTOP, Université du Québec À Montréal, BP 8888, suc. Centre ville, Montréal, QC, H2V 3W8, Canada
2Département de Préhistoire MNHN, UMR7194 CNRS, 1 rue René-Panhard, 75013 Paris, France
3Ecole Normale Supérieure, Géologie, UMR8538, 24 rue Lhomond, 75231 Paris, France
4IPGP, UMR7154, 1 rue Jussieu 75238, Paris, France.
5Université Moulay-Ismaël, BP 141, Errachidia, Maroc.

In southwestern Morocco (northern Sahara border) hydrothermal travertine deposits (CaCO3) occurred covering several km² with a thickness up to 15m. The main interest in dating such deposits is that travertine formations are generally regarded as remnants of Quaternary humid phases. A continuous core of 12 m mainly consisting of pure CaCO3 alternating with detrital layers of clay was sub-sampled for U-series dating (pure CaCO3) and for magnetic properties in layers rich in detritus. The magnetic record results indicated two main features: 1) normal polarity inclinations with a mean value around 40° is found for all measured samples from surface until 9.03 meter deep and 2) at 9.05 meters deep, reverse polarity inclinations abruptly appear with a mean inclination value around –40°. This polarity inversion was attributed to the Brunhes-Matuyama transition.

U-series dating indicates that samples from the top of the core up to 5.6 m yield ages (230Th/234U), (234U/238U) compatible with stratigraphy ranging between 500 ka and present-day. On the other hand, all samples below the depth of 5.6 m indicate infinite ages implying that secular radioactive equilibrium is reached from this depth down. However, samples above 5.6 m that yielded finite ages allowed us to calculate an initial (234U/238U)0 value for the hydrothermal fluid from which the CaCO3 was precipitated. This calculation was also carried on samples collected in outcrop or section near the coring site that gave calculable ages. Compiling these initial values, the frequency histogram of (234U/238U)0 shows an almost unimodal distribution with a mean value of 5 ± 0.5 for all samples (< 500 ka). Assuming this value constant before 500 ka, we calculated the time needed for the (234U/238U)0 of samples to reach the measured one for the samples older than 500 ka. The decay of 234U excess depends on its half-life (245.2 ± 0.49 ka) and may allow to date up to 10^9 y. We find an age of 800 ± 50 ka for samples located at depth between 8 and 10 m. This age is in agreement, though less precise, than the age of Brunhes-Matuyama transition of 780 ka.

Two easy methods in evaluation of an exploration data set

R. GHAVAMI-RIABI1*, R. KHALO-KAKAI1 and H. ASADI-HARONI2

1Mining, Petroleum and Geophysics Faculty, Shahrood Univ. of Tech, 7 Tir square, Daneshgah Bolv. (*correspondence: rghavami2@yahoo.com)
2Mining Engineering Dept., Isfahan Univ. of Tech., Khomeini shahr Bolv.

Mineralized factors and data

There are two type of statistical analyses for an easy and rapidly evaluation of an exploration data set. It is possible to evaluate and separate the mineralized and pathfinder elements in an exploration data set by using the discrimination and correspondence analyses [1,2,3]. The results of the two method confirm each other for a data set in the study area (Fig. 1 A and B) [4]. The data will be separated into a few sub-populations, if there are a few source of variation in the concentrations (Fig. 1-A). The anomalous sample numbers could distinguish by using correspondence analysis (Fig.1-B).

Conclusion

It is important to identify the source of anomaly in a data set, paragenetic parameters, and separation of the highly and relatively anomalous data in an exploration or envirnomental evaluation. These aims could be accessible by using discrimination and correspondence analyses together.

ArSENite oxidation by indigenous bacteria in the Bengal Delta Plain Aquifers (West Bengal, India)

DEVANITA GHOSH1, JOYANTO ROUTH2 * AND PUNYASLOKE BHADURY1

1Dept of Biological Sciences, IISER Kolkata, Mohanpur - 741252, Nadia, West Bengal, India
2Dept. of Earth Sciences, IISER Kolkata, Mohanpur - 741252, Nadia, West Bengal, India
(*correspondence: joyanto.routh@iiserkol.ac.in)

Microbial oxidation of arsenite occur in numerous phylogenetically distinct microorganisms, which play a role in As cycling by converting arsenite to the more strongly sorbing, less mobile, and toxic arsenate species[1].

We are studying biogeochemical processes associated with As cycling in Barbakpur village, Rahamatpur block, West Bengal – a region severely affected by high (up to 1 mg/l) As concentrations in groundwater. Water and sediment samples were collected to isolate microorganisms oxidizing arsenite. A new set of primers was designed based on amino acid alignments of several published arsenite oxidase subunit B (AroB) genes [2]. Besides, eubacterial 16S rRNA primers were also used to study the microbial communities. AroB-like sequences were detected in three wells. Molecular phylogeny based on AroB and 16S rRNA sequences reveal the presence of diverse bacterial groups. In addition, ongoing geochemical studies focus on characterizing the organic matter in sediments, which sustain these heterotrophs, arsenite speciation, and trace metal analyses [3].


Stability of phase D at high pressure and temperature: Implications for the role of fluids in the deep mantle

SUJOY GHOSH AND MAX W. SCHMIDT

Institute of Geochemistry and Petrology, ETH Zurich, Switzerland (sujoy.ghosh@erdw.ethz.ch)

Water is transported into the Earth’s interior via hydrous phases in descending slabs. Numerous high-pressure studies have clarified that several dense hydrous magnesium silicates (DHMS) are stable at mantle conditions in model compositions [1, 2]. These phases act as water carriers in the subducting slab and may play a critical role in water cycling in the Earth’s history and partial melting in the deep mantle. Among these DHMS, phase D is the DHMS phase hosting water in the lower part of the transition zone (where slab may travel along the upper/lower mantle boundary) carrying H2O from the upper to the lower mantle.

In the present study, we report data on the melting phase relations of phase D and of phase D + olivine + enstatite in (i) MgO-SiO2-H2O system (ii) with Al2O3 and (iii) with Al2O3 + FeO added in proportions appropriate for the mantle. Stochiometric oxide mixtures of brucite and quartz of phase D composition were used as starting material. Multianvil experiments were carried out at pressures between 22 and 24 GPa at temperatures between 1000 and 1800 °C using 10/3.5 pressure assembly.

Our data show that phase D decomposes to MgSi-ilmenite + stishovite + melt or MgSi-perovskite + stishovite + melt and indicate that phase D can be stable along a slab geotherm up to the base of the upper mantle for a range of H2O contents. Melt compositions are strongly magnesian with Mg:Si ratio of 1.5-5.2. Furthermore, mass balance calculation of the phase D composition experiments (with Al, Fe) composition suggests that melts can contain ~ 34 wt% H2O which fits well with EPMA analysis. The data are used to determine the stability of phase D, the proportions of melt formed during melting, the composition of the partial melts and the variation in the melt composition at different pressure temperature conditions. Upon thermal relaxation (to adiabatic temperatures)of a slab travelling along the 660 km discontinuity, phase D would melt releasing a H2O-rich magnesian melt from the slab. At present experiments at 32 GPa are under way to constrain the P-T slope of the melting.

Impact of groundwater composition and diffusive transport limitations on uraninite stability

D.E. GIAMMAR1*, J.M. CERRATO1, C.J. BARROWS1, Z. WANG1, V. MEHTA1, J.S.-LEZAMA-PACHECO2 AND J.R. BARGAR2

1Department of Energy, Environmental and Chemical Engineering, Washington University, St. Louis, MO 63130, USA (*correspondence: giammar@wustl.edu)
2Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, CA, USA

The long-term stability of biogenic uraninite in sediments and groundwater are important to the performance of in situ bioremediation strategies for uranium-contaminated sites. Stability is influenced by subsurface biogeochemistry, structure and composition of uraninite (UO2), and coupling with pore scale transport processes. Laboratory measurements of UO2 dissolution rates under well-mixed and diffusion-limited regimes were integrated with direct characterization of the solid phase to investigate the effects of groundwater cations on UO2 stability.

Groundwater contains abundant ions that can moderate U release from biogenic uraninite. Experiments were performed with Ca2+ and Zn2+ as model non-redox active groundwater cations with differing affinities for adsorption to metal oxides. Calcium only slightly inhibited UO2 dissolution, but zinc had a much greater inhibitory effect. Complementary sorption experiments verified that Zn2+ adsorbed more strongly than Ca2+ to the uraninite surface. The inhibition of dissolution by the cations is orders of magnitude stronger for oxic conditions than for anoxic conditions, which suggests that the adsorbing or surface-precipitating cation is acting to block the access of oxygen to the UO2 surface or inhibit the electron transfer from the UO2 to a soluble oxidant. The molecular-scale structure around calcium and zinc species present at UO2 –water interfaces were determined using X-ray absorption spectroscopy.

To examine UO2 dissolution under diffusion-limited conditions, experiments separated the reacting UO2 from the bulk solution by placing it in a tube covered with a membrane that allowed diffusive exchange of solutes. Slower net release rates of uranium from the tubes were caused by modest diffusive limitations to oxygen transfer to the UO2. Experiments were performed in both simple aqueous solutions and synthetic groundwaters to further explore the role of groundwater cations on the dissolution process.

Cu speciation in coastal waters using a vibrating gold microwire electrode

K. B. GIBBON-WALSH, P. SALAÜN AND C.M.G. VAN DEN BERG*

Marine Electrochemistry, School of Environmental Sciences, University of Liverpool, Liverpool, L69 3GP, UK (*correspondence: vandenberg@liv.ac.uk)

Cu speciation by pseudopolarography

Pseudopolarography (PP) was developed and optimised for use on a vibrating gold microwire electrode with the intention of developing a more sensitive technique for the speciation of Cu in seawater, with potential for in-situ application. The method was optimised and a desorption potential and conditioning sequence improved the electrodes reproducibility. Model ligands, including glutathione and other well characterised ligands [1] were studied in order to estimate the strength and class of Cu complexing ligands in Liverpool Bay.

Figure 1: On-board PP analysis in oxygenated coastal sea water (Liverpool Bay)

Cu pseudopolarograms performed on-site, in coastal sea water from Liverpool Bay always show a succession of waves (Fig 1.). The most positive wave corresponds to free+labile Cu complexes while wave II and III represents more strongly bound complexes. Only minor variations were observed between filtered/unfiltered sample and oxygen is not an interference highlighting the potential of the technique to be used in-situ.

Quantifying biotic responses to past abrupt climate change:
Thresholds and sensitivities

S.J. GIBBS1*, K.M. EDGAR1,2, P.R. BOWN3, S.A. O’DEA4,
A. SLUIDS4, B.H. MURPHY3 AND J.C. ZACHOS5

1School of Ocean and Earth Sciences, National Oceanography Centre, Southampton, SO14 3ZH, UK
(*correspondence: sxg@noc.soton.ac.uk)
2School of Earth and Ocean Sciences, Cardiff University, CF10 3AT, UK.
3Department of Earth Sciences, University College London WC1E 6BT, UK.
4Biomarine Sciences, Institute of Environmental Biology, Utrecht University, The Netherlands.
5Department of Earth and Planetary Sciences, University of California, Santa Cruz, CA 95064, USA.

Paleogene hyperthermals represent transient global warming events associated with massive carbon injection into the ocean-atmosphere system. Because the rate and magnitude of carbon release varied between the events, they are natural experiments ideal for exploring the relationship between carbon cycle perturbations, climate change and biotic response. Here we investigate how we can quantifiably compare biotic responses to events of differing magnitudes and environmental character, to utilise the wealth of high-resolution microfossil data emerging across a range of climate change scenarios. We quantify marine biotic variability through several hyperthermals from 56 to 40 million years ago, using records of evolutionary turnover and assemblage variance. Microfossil records from the biologically and functionally distinct plankton groups show a linear relationship between assemblage variability and the magnitude of carbon cycle perturbation during the various hyperthermals. These Paleogene plankton data show threshold behavior and scaled response to environmental changes associated with carbon cycle perturbations reflecting behaviour likely inherent in planktonic ecosystems and may suggest future biotic response may scale at least in a similar way to the hyperthermals.

Experimental investigation of the differentiation of iron-rich peralkaline magma

CHRISTOPHER GIEHL*, RAINER BABIEL, STEPHAN REICHE, MICHAEL MARKS AND MARCUS NOWAK

Institute for Geosciences, Eberhard-Karls-University, 72074 Tuebingen, Germany
(*correspondence: christopher.giehl@uni-tuebingen.de)

In this study we investigate the magmatic differentiation of peralkaline Fe-rich phonolitic melts. These are highly evolved compositions ((Na+K)/Al ratios >1) and are believed to be differentiated from mantle-derived alkali basaltic and nephelinitic sources. The studied composition (FeOtot = 11.6 wt%, #Fe = 0.98, (Na+K)/Al = 1.46) resembles a dyke rock, which is a potential source magma for parts of the Ilimaussaq peralkaline nepheline syenite complex, South Greenland [1].

However, the liquid line of descent of such Fe-rich phonolitic compositions is not well understood because of a lack of experimental data. Therefore, we performed crystallization experiments with synthetic glass as starting material at 1 kbar and 950 to 750°C. We used hydrothermal rapid quench vessels and covered a wide range of water activities and oxygen fugacities using gold capsules and graphite-lined gold capsules. To achieve near-equilibrium conditions, run times of 4 hours were sufficient for H2O-saturated experiments, in nominally anhydrous experiments run times of 3 weeks were necessary. H2O-saturated experiments reproduce only parts of the observed early magmatic phases of the dyke rock (sp + cpx). In contrast, under nominally anhydrous and more reducing conditions, the complete early magmatic phase assemblage of the dyke rock (sp, cpx, ol, afs, ne) and an alkali-rich residual melt ((Na+K)/Al = 1.65) was successfully reproduced at and below 850°C. Experiments already conducted were carried out using an equilibrium crystallization approach. Upcoming experiments will simulate fractional crystallization using multi-step differentiation to elucidate the complex differentiation process due to the unusually large temperature interval of crystallization suggested for such magma compositions.

Dust particles in bronchoalveolar lavage fluids from coal miners in Quang Ninh province, Viet Nam

R. GIERÉ*, T.B. HOÀNG-HÒA AND K.P. SEDLAZECK
Albert-Ludwigs-Universität, 79104 Freiburg, Germany
(*correspondence: gier@uni-freiburg.de)

Inhalation is the most important pathway for airborne particles into the human body. The pulmonary system provides an efficient filtering mechanism, which retains most of the coarse particles in the nasal and oral cavities. The fine-particle fraction (<2.5 µm aerodynamic diameter) penetrates deeper into the respiratory tract and reaches the alveolar region. Here, the particles remain for long periods of time and interact with lung fluid and tissue. The deepest part of the lungs, thus, acts a special type of active sampler for atmospheric dust. The deposited particles can be studied in tissue samples or in bronchoalveolar lavage (BAL) fluids.

This investigation aims at characterizing mineralogically and chemically the particles in BAL fluids, which were retrieved from coal miners in the Quang Ninh province, northern Viet Nam. The BAL fluids were filtered to recover the solid fraction, which was dried and studied by X-ray diffraction (XRD). The main mineral component is halite, an artefact from the sterile saline solution (0.9 wt% NaCl, heated to 37 °C) used during the lung lavages. One of the samples also contains thenardite (Na2SO4) and gibbsite (Al(OH)3).

To remove halite, all samples were rinsed repeatedly with deionized water, filtered and dried, and then subject to further investigations. These residues contain the following main components (in wt%): C = 3.3–4.8; Al = 1.7–7.4; Si = 24–94; and Fe = 0.7–1.2. Minor amounts of Na, Mg, S, K, Ca, Cr, Zn, Cd, Ba and Pb are also present, whereas Ni, Cu, As, and Sb were not detected.

XRD analysis of the washed residues revealed that they contain primarily quartz and gibbsite. We are currently using scanning electron microscopy, combined with energy-dispersive X-ray spectroscopy (SEM-EDX), to collect quantitative data on the mineralogical composition of these residues. So far, we have detected the following additional phases: clay minerals, Cr-Fe(Ni)-alloys, K-feldspar, Fe-sulfides, Fe-oxides/hydroxides, gypsum, calcite, dolomite, fly ash spheres, and coal particles. One of the residues also contains Mg-silicates, indicating that the coal miner may have worked in a silicate mine in the past.

Through BAL analysis it is thus possible to deduce the occupational exposure of subjects. This technique could also be applied to humans living in areas with high levels of particulate pollution to identify the main particle sources.

Origin of the differences in redox reactivity of iron (oxyhydr)oxides revealed by time-resolved spectroscopy

B. GILBERT1*, J. E. KATZ2, X. ZHANG3, K. ATKENKOER3, C. FRANDSEN4, PIOTR ZARZYCKI5, KEVIN M. ROSSO5, R. W. FALCONE1 AND G. A. WAYCHUNAS1
1Lawrence Berkeley National Laboratory, Berkeley CA USA. (*correspondence: bgilbert@lbl.gov)
2Denison University, OH USA.
3Argonne National Laboratory, Argonne, IL USA.
4Department of Physics, Technical University of Denmark
5Pacific Northwest National Laboratory, USA.

The redox chemistry of nanoscale transition metal oxides, hydroxides and oxyhydroxides is of central importance to broad areas of the Earth sciences, including soil and marine biogeochemistry, contaminant remediation, and paleoclimate records. Iron-bearing phases are the most important redox-active minerals in nature and the complex chemistry of these materials exemplifies the challenges in understanding solid phase redox reactions. For example, following the exposure of ferric iron (Fe3+) (oxyhydr)oxides to reducing agents, interfacial electron transfer (ET) can lead to several transformation pathways including release of soluble ferrous iron (Fe2+) (dissolution), formation of alternative ferric or mixed valence phases (transformation), or particle growth. Understanding and predicting such redox processes will require the application of time-resolved methods capable of observing the intermediate species that control reaction path.

We have applied an optical-pump–X-ray-probe method with subnanosecond time resolution to study the fate of ferrous iron sites formed by electron injection at the surface of three phases of ferric iron (oxyhydr)oxides. We used this approach, combined with conventional kinetics studies, to distinguish the timescales for the elementary redox processes occurring during the reductive dissolution of 6-line ferrihydrite, maghemite and hematite nanoparticles. For each phase we quantified the rates of Fe-to-Fe electron hopping, the rates of interfacial electron transfer, the lifetime of kinetic electron trapping within the nanoparticles, and the rates of the full reaction including ferrous iron release into solution. Comparison of these rates which span from the nanosecond to the second scale reveal new insights into the electronic and structural factors controlling the redox reactivity of these phases.
Mapping the amorphous-to-crystalline transitions in CaCO₃ biominerals with 20-nm resolution

P.U.P.A. GILBERT
Departments of Physics and Chemistry, University of Wisconsin, Madison, WI 53706, USA
(pupa@physics.wisc.edu)

One of the most fascinating aspects of calcite biominerals are their intricate and curved morphologies, quite different from the normal rhombohedral crystal habit of geologic calcite. These morphologies are achieved via amorphous precursor mineral phases [1]. In this talk we will show that in sea urchin larval spicules two distinct phase transitions occur, 1→2 and 2→3 [2]. The 1→2 transition is regulated by inhibiting proteins, while the 2→3 is thermodynamically driven, and occurs spontaneously [3].

Figure 1: Cross-section of a 48-h sea urchin larval spicule, caught in the act of transforming from ACC (type 1 = red, type 2 = green) to crystalline calcite (type 3 = blue), and with imaged XANES-PEEM spectromicroscopy.


Natural and artificial noble gases as tracers of injected CO₂ migration within a deep reservoir

STUART GILFILLAN1*, R. STUART HASZELDINE1, ROBERT POREDA2 AND SUSAN HOVORKA3

1Scottish Carbon Capture and Storage, University of Edinburgh, UK.  
(*correspondence: stuart.gilfillan@ed.ac.uk)
2Department of Earth and Environmental Sciences, University of Rochester, New York, USA.  
3Gulf Coast Carbon Center, Bureau of Economic Geology, University of Texas at Austin, Texas, USA.

CO₂ capture and subsequent geological storage of CO₂ is gaining momentum as a means of economically abating anthropogenic CO₂ emissions from point sources. For the technology to be universally deployed it is essential that a robust, reliable and inexpensive means to trace the migration of CO₂ within the subsurface exists. Monitoring during injection will increase confidence that the site characteristics were correctly determined and met. Furthermore, should migration and subsequent surface leakage occur, the ability to track origin and ownership of CO₂ at near and ground surface will be critical for remediation purposes.

As an analogue for tracing CO₂ migration within an engineered storage site, this presentation will examine both natural and artificially injected noble gases at the SECARB early project at Cranfield in MS, USA. Natural CO₂ rich in mantle derived noble gases was injected into a portion of the reservoir via a deep injection well and samples were collected via U-tube sampling equipment from two nearby observation wells. Additionally, two separate injections of artificial Kr and Xe tracers injected with the CO₂ were undertaken.

Noble gases are conservative tracers within the subsurface, proving to be invaluable in determining both the origin of CO₂ and how it is stored in natural CO₂ reservoirs [1,2]. This presentation will compare measurements of the natural ³He/⁴He, CO₂/³He, ³He, ⁴He, Ne and Ar concentrations within the reservoir prior to CO₂ breakthrough with those after CO₂ arrival at the observation wells. We show that a component of the He fingerprint observed in the injected CO₂ can be clearly traced in both observation wells. Additionally, we see a clear spike in Kr and Xe concentrations following CO₂ breakthrough. Our results show that CO₂ can be traced within a storage site using noble gases, illustrating significant potential for monitoring CO₂ migration in future engineered storage sites.

High-precision Pb isotopes have become useful in discovering segment-scale (<100 km) heterogeneity in MORB sources. Here I describe how this heterogeneity co-varies with other isotopes and with major and trace elements within a 10-km long “4th order” segmentation of the axial magma chamber at the Endeavour segment of the Juan de Fuca Ridge, and how this heterogeneity is passed on to hydrothermal systems. Basalts in the one km-wide axial valley at Endeavour are characterized by large (3 to 4-fold) variations in their K/Ti, Zr/Nb, and La/Yb ratios at 7-8% MgO. Variations in Sr, Nd, and Hf isotopes are small (<0.0001) but correlate with the element ratios. Variations in Pb isotopes are larger ($^{206}$Pb/$^{204}$Pb = 18.4-18.9) and therefore more useful. Pb correlations lie below the NHRL. $^{206}$Pb/$^{204}$Pb correlates best with HFSE-enrichment, especially Nb. That correlation differs from what is seen along the southern JdFR and EPR, and defines a type of mantle enrichment specific to the northernmost JdFR. This enriched mantle only began to be tapped within the last ~30 Ka. Qualitatively, I attribute the enrichment to a young pyroxenitic source with a lower solidus than the surrounding peridotite, and with “C”-type isotopic characteristics. The Pb in the vigorous hydrothermal systems at Endeavour is entirely basalt-sourced, without evidence of sediment, which leaves the anomalously high CH$_4$ and NH$_3$ in the hydrothermal fluids unexplained. Preliminary results indicate differences in Pb isotopes between hydrothermal fields a few km apart. This may help to map their recharge zones and the integrated architecture of the basaltic crust.

The formation of free radicals on sulphide and silicate mineral surfaces [1,2] is a relevant topic due to its great importance in the treatment of mine wastes, geomedicine and, more recently, as an hypothetic oxidation pathway on Mars and Early Earth [3]. Although the atomic mechanisms involved in mineral surface reactions are relatively well understood, the kinetics pathways as well as the time extent of these reactions in natural environments have not yet been well characterized.

In this work, the kinetics of H$_2$O$_2$ generation at mineral–water interface was monitored with real time microelectrode measurements. Experiments were performed under continuous stirring by using aqueous slurries of pyrite, antigorite, olivine, and glauconite, as sample probes, in both oxic and anoxic conditions.
Evaluation of thermodynamic data and activity coefficient models for the geochemical modeling of CO₂ storage systems

M.J. Gimeno*, P. Acero, V. Gutiérrez, L.F. Auqué, M.P. Asta and J. Gómez

Earth Sciences Dpt., University of Zaragoza, Spain
(*correspondence: mjgimeno@unizar.es, patriace@unizar.es, vane_rodrigo@hotmail.com, lauque@unizar.es, mpastai@unizar.es, jgomez@unizar.es)

The selection of adequate CO₂ geological storage systems and the evaluation of their storage capacity and behavior rely largely on geochemical modeling, whose results are strongly dependent on the selection of appropriate thermodynamic data and approaches.

In this study, two groups of geochemical calculations were carried out to gain insight into the influence of those issues. In the first group of calculations, the saturation state of several dilute groundwaters with respect to different mineral phases potentially relevant in geological storages for CO₂ was assessed by using different geochemical codes and thermodynamic databases. For the second group of calculations, the geochemical evolution in the direct vicinity of a hypothetical well during the desiccation caused by the injection of supercritical CO₂ into two types of saline aquifers was simulated with the assistance of the PHREEQC code (Parkhurst and Appelo, [1]) by using two different databases and approaches for the calculation of activity coefficients included with the code: (1) the Watqua4f.dat database with an ionic association approach, and (2) an improved version of the pitzer.dat database with the specific ion interaction approach developed by Pitzer [2].

In the calculations for the dilute groundwaters, significant differences in the saturation indexes are only obtained for minerals for which varieties with different cristallinity are included in the databases (remarkably for dolomite). For the modelling exercises focused on the evolution of saline waters, the main differences between the results obtained by the two model approaches described above, are mainly related to the order and desiccation degree at which different mineral phases precipitate and to the amounts of precipitated minerals throughout the simulations.


Age and origin of alkaline lavas from Tore-Madeira Rise: Interactions between complex lithosphere motion and multi-components source

J. Girardeau¹, R. Merle²*, A. Marzoli³ and M. Chiaradia³

¹Université de Nantes, 2 rue de la Houssinière, 44322 Nantes, France (Jacques.Girardeau@univ-nantes.fr)
²Università di Padova, via Gradenigo 6, 35100 Padova, Italia (*correspondence: renaud.merle@unipd.it; andrea.marzoli@unipd.it)
³Université de Genève, 13 rue des Marañchers, 1205 Genève, Switzerland (Massimo.Chiaradia@unige.ch)

The Tore-Madeira Rise (TMR) is an alignment of seamounts of 1000×50 km oriented SSW-NNE, extending from the Tore seamount, located 300 km west of Lisbon, to the archipelago of Madeira. Here, we document the petrology, geochemistry and isotopic characteristics of TMR lavas from 22 dredging sites, located on 13 seamounts and 5 localities on Tore seamounts. The exclusive occurrence of alkaline lavas (mafic and differentiated) substantiates the importance of alkaline magmatism in the TMR edification. The dredged basalts display typical OIB-like incompatible elements and REE characteristics similar to those observed in Madeira basalts. Reliable ⁴⁰Ar/³⁹Ar and U/Pb ages suggest five magmatic phases on the TMR and surrounding areas that can be related to the motion of the Iberian plate. No specific isotopic characteristics can relate to a given magmatic phase. Regardless of their age, the Pb isotopic compositions of the basaltic rocks plot below the NHRL, in the field of the Madeira archipelago lavas while the differentiated lavas display a trend from this field toward high ²⁰⁷Pb/²⁰⁴Pb which is interpreted as a contamination by the sub-continental lithospheric mantle (SCLM) of the Iberian margin. This precludes the involvement of two distinct mantle plumes (Canary and Madeira) in the genesis of the TMR lavas, as previously suggested. The isotopic composition of the basaltic lavas requires at least three distinct components. The main isotopic characteristics are related to a mixture between a depleted asthenosphere-like mantle and a HIMU-like component. The contribution of an EMI-like component is also required in particular to explain the isotopic characteristics of the Seine-Isabelle-Godzilla seamounts. Considering the position of these seamounts close to the southern branch of the Azores-Gibraltar Fracture zone, we interpret this EMI-like component as due to a sliver of SCLM trapped in the asthenosphere. However, this SCLM is distinct to those involved in the genesis of the differentiated samples.
Insights into marine microbial communities that couple anaerobic biogeochemical cycles to remote oxidants

PETER R. GIRGUIS1*, PENGFEI SONG2 AND MARK NIELSEN2

1Harvard University, 16 Divinity Avenue Room 3085, Cambridge, MA 02138 (* correspondence: pgirguis@oeb.harvard.edu)
2Harvard University, 16 Divinity Avenue Room 3092, Cambridge, MA 02138

Extracellular electron transfer (EET) is a process whereby microbes shuttle electrons outside the cell, and access solid-phase oxidants as well as spatially remote oxidants. EET has been well-studied in cultivated microbes, e.g., heterotrophic iron-reducing “-proteobacteria. The relevance of EET in nature, however, and its impact on biogeochemical cycles remains poorly constrained. Anaerobic marine sediments host microbial communities that are involved in numerous biogeochemical cycles, and those capable of EET would have access to solid-phase as well as remote oxidants. Here we present the first comprehensive data on the population structure and functional potential of marine bacteria associated with EET. These communities were recovered from two systems: the anode of a bioelectrochemical system (BES) deployed in marine sediments in situ, and a BES deployed in high temperature hydrothermal vents. These communities were dominated by distinct groups of Proteobacteria and Fusobacteria. Metagenomic analyses and geochemical considerations suggest that they are participating in a complex sulfur cycle that includes the recycling of sulfur among oxidizers, reducers and disproportionators. Unexpectedly, these analyses revealed numerous other physiological capacities. These data suggest that microbial EET is likely more widespread than previously considered, and the functional potential of these communities requires us to reconsider the canonical view of anaerobic sediment biogeochemistry. If these microbial metabolisms are coupled to remote oxidants such as oxygen and nitrate via EET, the biogeochemical cycling of these elements will likely be more vigorous than previously recognized (as these reactions become more thermodynamically favorable). The findings presented herein provide a plausible explanation for some previously observed elevated rates of recalcitrant carbon degradation, and underscores the need for further investigation into the relevance of EET to global biogeochemical cycles.

Aerobic hydrogen oxidation by a chemolithotrophic *Beggiatoa* strain

A.-C. GIRNTH* AND H.N. SCHULZ-VOGT

Max Planck Institut for Marine Microbiology, Celsiusstraße 1, 28357 Bremen, Germany
(*correspondence: acgirnth@mpi-bremen.de)

Hydrogen oxidation in oxic/anoxic gradients

Transition zones between oxic and anoxic environments are primary habitats for aerobic hydrogen oxidizers. In sulfidic sediments, filamentous bacteria of the genus *Beggiatoa* thrive within this narrow horizon and feature fine-tuned chemotactic responses to keep track of the interface. So far, only anaerobic hydrogen oxidation coupled to reduction of stored sulfur has been shown for a heterotrophic *Beggiatoa* strain [1]. Here we demonstrate aerobic hydrogen oxidation by the chemolithoautotrophic strain *Beggiatoa* 35Flor grown in a mineral medium featuring artificial oxygen, sulfide and hydrogen gradients.

*Beggiatoa* 35Flor uses hydrogen as an accessory electron donor

In the presence of hydrogen, *Beggiatoa* 35Flor mats exhibit higher oxygen consumption once the sulfide flux decreases, as indicated by a shorter distance of the mats to the air/agar interface. Microsensor profiles show that low hydrogen fluxes are continually and fully oxidized within the oxic region of the *Beggiatoa* mat. Higher hydrogen fluxes have initially a more pronounced influence on the mat position, but oxidation ceases after a few days for a yet not determinable reason. A gene encoding for the large subunit of a hydrogen uptake hydrogenase was retrieved from strain 35Flor. Supply with fixed nitrogen compounds does not impair the hydrogen-oxidizing capacity of this nitrogen-fixing strain, suggesting that the hydrogenase is regulated independently of the nitrogenase. This result indicates that hydrogen is used as an electron donor and not merely oxidized for energy recycling. All attempts to grow the strain 35Flor with hydrogen as the only electron donor failed so far. Our findings show that the strain *Beggiatoa* 35Flor is capable of aerobic hydrogen oxidation when grown in gradient medium imitating its natural habitat. However, hydrogen appears to serve only as an accessory electron donor since growth on hydrogen alone could not be achieved.

The ash that closed Europe’s airspace: Part I, grains size distribution of the Eyjafjallajökull ash and soluble salt coatings

S.R. GISLASON1*, E.S. EIRIKSDOTTIR1, H.A. ALFREDSSON1, N. OSKARSSON1, B. SIGFUSSON2, G. LARSEN1, T. HASSENKAM2, S. NEDEL2, N. BOVET2, C.P. HEM2, Z.I. BALOGH2, K. DIDERIKSEN2 AND S.L.S. STIPP2

1Institute of Earth Sciences, University of Iceland, Reykjavik, Iceland; (sigrg@raunvis.hi.is)
2Nano-Science Centre, Department of Chemistry, University of Copenhagen, Denmark; (stipp@nano.ku.dk)
3Reykjavik Energy, Iceland.

On 14 April 2010, when magma from the Eyjafjallajökull volcano intruded glacier-meltwater, an explosive phreato-magmatic eruption sent unusually fine-grained ash into the jet stream. It quickly dispersed over Europe. Reported airplane encounters with ash have caused sand blasted windows and melting of particles inside jet engines, causing them to fail. Therefore, air traffic was grounded for several days. Concerns also arose about health risks from fallout, because ash can transport acids as well as toxic compounds. Most studies on ash are made on post-eruptive material that have mixed with other atmospheric particles and suffered exposure to water as rain or fog, which would alter surface composition. In this study, a unique set of dry ash samples was collected during the explosive eruption and compared with fresh ash with the same bulk composition from a later more typical magmatic event, when meltwater did not have access to the magma.[1]

Up to 70 mass % of the phreato-magmatic ash particles, collected 50 km from the source, was <60 µm in diameter, 22% was <10 µm and 11% was z 4.4 µm. The finest grain size was found in the centre of the plume. The magmatic ash was coarser and its surface area was an order of magnitude smaller than for the explosive ash. The relative concentration of surface salts was significantly lower on the explosive ash than the magmatic ash, because less volatile compounds were available to condense on the surfaces when water and steam were present. Instead, they dissolved in the meltwater and were transported as solutes in the ensuing floodwaters. The surface salts dissolved rapidly when exposed to experimental and natural waters, releasing pollutants and nutrients. Some of the salts further enhanced bulk dissolution of the ash.

This paper is the first of a two part presentation, where the second part, by Susan Stipp, focuses on the characteristics of the nanoparticles.


The effect of time and climate on volcanic soil formation

S.R. GISLASON1, E.S. EIRIKSDOTTIR1, H.A. ALFREDSSON1, B. SIGFUSSON2, M.T. JONES1 AND E.H. OELKERS3

1Institute of Earth Sciences, University of Iceland, Reykjavik, Iceland; (sigrg@raunvis.hi.is)
2Reykjavik Energy, Iceland.
3GET-Université de Toulouse-CNRS-IRD-OMP, 14 Avenue Edouard Belin, 31400 Toulouse, France

Andosols, soils derived from volcanic material, cover about 1.9% of the terrestrial surface and store about 4.9% of the Earth’s carbon [1]. Andosols cover most of the volcanic islands on Earth. These soils are fertile, most of the islands are heavily populated and much of the river suspended matter delivered to the ocean stems from these islands. To a great extent, the soil is formed from air borne volcanic ash, preventing nutrient depletions with time, but making it prone to mechanical erosion.

In the days, weeks and months after deposition of air borne volcanic ash, nutrients and pollution will migrate into the soil at elevated rates. This is caused by soluble metal and proton salts coating the volcanic ash that dissolve orders of magnitude faster than the bulk volcanic ash that is mostly glass. Between these periodic fluxes of dissolved elements, weathering and erosion rates are primarily governed by climate, lithology, average rock age, topography and vegetation cover. A detailed study of catchments in NE Iceland shows that for each degree of temperature increase the runoff, mechanical weathering flux, and chemical weathering fluxes in these catchments have been found to increase from 6 to 16%, 8 to 30%, and 4 to 14% respectively, depending on the catchment [2]. These results demonstrate a significant feedback between climate and Earth surface weathering on the timescale of years to millions of years [3], and suggest that weathering rates are currently increasing with time due to global warming.

Effect of alkali content and Fe oxidation state on the S oxidation state and solubility in rhyolitic glasses

G. GIULI1*, E. PARIS1, R. ALONSO MORI2, P. GLATZEL2, M.R. CICCONI1, B. SCAILLET3 AND S.G. EECKHOUT2

1School of Science and Technology, Geology division, University of Camerino, ITALY
2European Synchrotron Radiation Facility (ESRF), Grenoble, France
3Inst. de Sciences de la Terre D’Orleans, UMR, CNRS-UO, Orleans, France

The Fe oxidation state, coordination geometry and <Fe-O> distances have been determined by Fe K-edge XANES and EXAFS for a set of sulphur bearing silicate glasses of rhyolite composition in the aim of determining: 1) the effect of bulk composition on the iron oxidation state and local structural environment;2) the effect of Fe oxidation state on sulphur behaviour in the corresponding magmas/melts. Glass compositions have been chosen so as to represent S- Cl- F bearing rhyolitic magmas with low to high alkali content. These glasses have been equilibrated at a range of different oxygen fugacity conditions typical of magmatic conditions and ranging from –15.4 to –10.75 log units (at 800 °C, 1.5 kbar). Comparison of the pre-edge peak data with those of Fe model compounds allowed to determine the Fe oxidation state and coordination number for all the glasses analysed. The Fe3+/Fe2+ ratio varies from 0.25 to 0.80 (±0.05) in the glasses studied. Moreover, pre-edge peak data clearly indicate that Fe 3+ can be present in [4] and/or [5] coordination according to the alkali content of the glass, whereas Fe 2+ is present in [5] coordination units for these compositions. The presence of minor amounts of [6] coordinated Fe cannot be ruled out by XANES data alone. EXAFS derived Fe-O distance in the most oxidised sample (Fe-O=1.85 Å) indicates that Fe3+ is in tetrahedral coordination. For these glass compositions, going from reducing to oxidising condition results in higher fraction of network forming [4]Fe3+, thus increasing the polymerisation of the tetrahedral network.Alkali content has been found to have a very strongly effect on the Fe oxidation state: at a given oxygen fugacity, Fe oxidation state increase noticeably with increasing alkali content. A direct proportionality has been found between the S2-/Fe2+ molar fractions. As Fe oxidation state is known to affect the solubility of S2- species in silicate melts, Alkali content is expected to play a major role together with oxygen fugacity in the S geochemical behaviour in silicate magmas.


Redox dynamics resulting from chemical and physical fluxes in surficial permeable sediments

B.T. GLAZER1*, J. FRAM1,2, J.L. MURPHY1, K. FOGAREN3 AND F.J. SANSONE1

1University of Hawaii, Department of Oceanography, 1000 Pope Rd., Honolulu, HI 96822;
(*correspondance: glazer@hawaii.edu)
2College of Oceanic and Atmospheric Sciences, Oregon State University, 104 COAS Administration Bldg

The upper layers of nearshore permeable sediments are dynamic, active sites of intense redox cycling. Previous research and our preliminary results indicate that vertical redox oscillations in these sediments can be driven by biogeochemical or physical variability, or by episodic events such as severe storms and their associated terrestrial runoff. Further, it can be assumed that each of these forcings operate on different and distinctive time and vertical scales. The current work focuses on central goals of calculating the fluxes of redox-sensitive chemical species in surficial permeable coastal sediments, and understanding the transformations within the highly responsive “zone of reactivity” in the upper centimeters of these sediments.

We have made extended deployments of a custom physical and chemical sensor package in nearshore permeable sediments, as part of a cabled seafloor observatory. Instrumentation includes a multi-channel high-resolution miniature thermistor chain, an in situ electrochemical analyzer (ISEA-III, AIS Inc.), a profiling micromanipulator, oxygen optodes (Aanderaa), independent temperature loggers (RBR), and a seafloor visualization system, all integrated into the existing physical sensor network observatory (Kilo Nalu Nearshore Reef Observatory, Oahu, Hawaii, USA). Here, we describe on-going work aimed at: (i) improving our understanding of the interaction between these active, carbon recycling sediments and the overlying water column; (ii) examining in detail the temporal and spatial variability of key redox-reactive chemical species; (iii) quantifying the relative contributions of benthic photosynthesis, sand ripple position, currents and waves to redox oscillations; and (iv) integrating fine-scale chemical measurements with porewater velocity modeling to calculate biogeochemical fluxes.
Mercury stable isotopic variations in Arctic Ocean pelagic sediment

JAMES D. GLEASON1, JOEL D. BLUM1, TED C. MOORE1, LEONID POLYAK2 AND MARTIN JAKOBSSON3
1 University of Michigan, Dept. of Geological Sciences, Ann Arbor, MI 48109, USA (*correspondence: jogleaso@umich.edu)
2 Ohio State University, Byrd Polar Research Center, Columbus, OH 43210, USA (polyak.1@osu.edu)
3 Stockholm University, Dept. of Geology and Geochemistry, Stockholm, Sweden (martin.jakobsson@geo.su.se)

Mercury isotopic compositions were measured in 14 samples of Arctic Ocean pelagic sediment from three sites: Lomonosov Ridge, Yermak Plateau and Mendeleev Ridge. Holocene-age sediment from 4 piston cores shows highly negative and variable mass dependent isotopic fractionation ($\delta^{202}$Hg = -1.06 to -2.98; +/-0.15‰). Surface sediment at two localities (Lomonosov Ridge and Yermak Plateau) shows small deviations from mass dependence recorded as $\delta^{201}$Hg = -0.11 to -0.14 (+/-0.10‰). In piston core 96/12-1pc (Lomonosov Ridge; 1003 m water depth; 87°05.9’N; 144°46.4’E), $\delta^{202}$Hg appears to decrease with depth in the core from surface ($\delta^{202}$Hg = -2.22) down to MIS 5.3 (~100 ka; 2 meters depth; $\delta^{202}$Hg = -2.98). Mercury concentrations (~3 ppb to 114 ppb) are not well correlated with Hg isotopic composition, and neither of these parameters appears to be correlated with the Mn-rich/Mn-poor cyclic banding in core 96/12-1pc, which is thought to record variations in Quaternary ventilation and/or ice conditions of the Arctic Ocean. Overall, the sediment Hg isotopic compositions likely reflect a variable provenance signal of mixed terrestrial and atmospheric Hg reservoirs supplying the Arctic Ocean. The enhanced negative $\delta^{202}$Hg signature in the modern Arctic sediments could be due to the influence of anthropogenic Hg from coal combustion, or from enhanced photochemical reduction and loss of Hg from modern Arctic surface waters due to reduced sea-ice cover.

Sulfate reduction and microbial abundance in saline, alkaline Lake Van (Turkey)

CLEMENS GLOMBITZA*, JENS KALLMEYER AND PALEOVAN SCIENTIFIC PARTY
University of Potsdam, Institute of Earth and Environmental Sciences, Karl-Liebknecht-Str. 24, 14476 Potsdam, Germany (*correspondence: clemens.glombitza@geo.uni-potsdam.de)

Lake Van is the fourth largest terminal lake in the world. It is located on the Eastern Anatolia High Plateau (Turkey) and surrounded by two semi-active volcanos (Nemrut Dagi and Syphan Dagi). Evaporation processes, chemical weathering of volcanic rocks and hydrothermal activity have created an environment of extreme alkalinity (155 m eqL⁻¹, pH 9.81) and salinity (21.4 ‰) [1]. Kempe and Degens [2] proposed an ancient Ocean with high alkalinity, a high pH and low Ca and Mg concentrations, analogous to modern soda lakes like Lake Van. This theory was and still is discussed controversially, e.g. Hardie [3] suggested that the post-Hadean ocean was never a soda ocean but instead a neutral-halide ocean. Recently, Shibuya et al. reported evidence for high alkaline fluids in an Archean subseafloor hydrothermal system resulting in reactive mixing zones between alkaline fluids and neutral seawater [4]. A detailed study of the currently ongoing microbial processes in Lake Van may provide the information necessary to interpret the signals from fossil ecosystems. Independent from the different opinions about early Ocean chemistry, this study explores an ecosystem that deviates considerably from typical freshwater or marine systems with regard to porewater chemistry and biogeochemical processes. We here report the first results from microbiological investigations (porewater chemistry, cell abundance and sulfate reduction rates) in samples from two sites (Northern Basin and Ahlat Ridge) at Lake Van, retrieved during the ICDP drilling campaign in summer 2010. Although located in relatively close proximity (7 km) sulfate reduction rates reveal unexpected differences between the two sites, indicating a high sensitivity of microbial activity to changes in hydrological conditions and organic matter input. Overall cell abundances deviate considerably from what is commonly observed in marine sediments.

Land use control of groundwater chemistry in the Pyosun Watershed, Jeju Island, Korea

YOUNG-HWA GO1, SEONG-TAEK YUN1*, KYUNG-GOO KANG2, BERNHARD MAYER3, KYOUNG-HO KIM1 AND HAE-NAM HYUN4

1Department of Earth and Environmental Sciences, Korea University, Seoul 136-701, South Korea
(*correspondence: styun@korea.ac.kr)
2Jeju Special Self-Governing Province Development Corporation, Korea
3Department of Geoscience, University of Calgary, Calgary, Alberta, Canada T2N1N4
4Department of Bioscience and Industry, Jeju National University, Jeju 690-756, South Korea

As groundwater from basaltic aquifers is a unique source of water supply in the volcanic Jeju Island, Korea, a better understanding of the current status of groundwater is important for a sustainable future water supply. For this study of the Pyosun Watershed located at the southeastern part of the island, we collected 90 groundwater samples from 45 existing wells and 41 soil water samples using porous cups installed at various depths at two sites. Hydrochemically, well groundwater was dominantly of the Na(-Mg-Ca)-HCO3(-Cl) type, while soil water varied between Na(-Mg-Ca)-Cl-HCO3(-SO4) type at an upgradient forested area to a Na(-Mg-Ca)-Cl type at a downgradient agricultural (orchard) area. Most ions in groundwater, especially NO3, Cl, SO4, Na, Ca and Mg, increased in concentrations in aquifers at low altitudes (about <150 m a.s.l.) where land use is dominated by orchards and rural developments. Nitrate concentrations of groundwater ranged from 0.4 to 23.3 mg/L (median 4.7 mg/L). The results of a Principal Component Analysis (PCA) of hydrochemical data indicates that two major processes (i.e., anthropogenic contamination and water-rock interaction) control the groundwater chemistry. Water-rock interactions were dominated by silicate weathering (as indicated by the increases of HCO3 and silica) with minor ion exchange and sorption. Combined with hydrochemical data, nitrogen and oxygen isotopes of groundwater nitrate (n=43) showed the systematic change of major nitrate sources, from nitrification in soil organic matter at upgradient forested and grassland areas to chemical fertilizers at the orchard areas to minor contributions of manure and sewage-derived nitrogen at low altitudes. Thus, careful control of fertilizer use is highly recommended for a sustainable management of future groundwater quality in the Pyosun Watershed.

Hydrochemical characteristics of Bigadiç (Balikesir) geothermal area, Turkey

GÜLER GÖÇMEZ1 AND ERDOĞAN ÖLMEZ2

1Department of Geology Engineering, Selcuk University, (gulergocmez@selcuk.edu.tr)
2Directorate of Mineral Research and Exploration of Turkey (erdogan_olmez@yahoo.com)

The study area is located in 57 km southwestern of Balikesir, West Anatolia, Turkey. The stratigraphy of the area is characterized by the presence of ophiolites of Mesozoic basement, covered by Tertiary aged Dedetep Formation (riodacite, dacite, tuff, agglomerate) and Quaternary covers. Major visible tectonic lines that control fluid flow in region is represented by faults approximately trending in N-NE direction; it determined the main morphological structure of the region. The chemical composition of water discharges clearly shows that the Bigadiç geothermal system produces similar types of fluids having travelled distinctly different paths. A plume of high HCO3 and SO4 waters feeds discharge area, bordered by two strike slip faults. EC values of hot and mineral water in region are range between 2100 and 3040 µS/cm, temperature is between 24 and 98 °C, total mineralization ranges from 2646 to 3537 mg/l, and pH values range from 6.4 to 8.3 and show generally the acidic character. Four wells in region were opened (HK-1: T=47 °C and Q=0.5 l/s; HK-2: T=98 °C and Q=60 l/s; HK-3: T=98 °C and Q=40 l/s; HK-4: T=94 °C and Q=10 l/s) to use in balneological purposes, space and greenhouse heating. The hot and mineral waters have “Rav waters” properties according to Giggenbach diagramme. The reservuar rock temperature is calculated due to geothermometers as 100 to 110 °C. The hot and mineral water is classified as B-F-Na-HCO3-SO4 according to AIH. High content of boron in fluids produced from the geothermal system throughout the volcanic environment, thought to be associated with extensional tectonics and volcanic hosted rocks leachings from the Bigadiç area appear to repr. All of these extensional type discharges from the Bigadiç area appear to represent geothermal fluids most directly derived from an environment dominated by riolitic/andesitic magmatism.
Recent advances in first principles based modeling and simulations of the physics and chemistry of large, complex atomistic systems

WILLIAM A. GODDARD, III

Charles and Mary Ferkel Professor of Chemistry, Materials Science, and Applied Physics Director, Materials and Process Simulation Center (MSC) California Institute of Technology (139-74) Pasadena, CA 91125

Advances in theoretical chemistry, computational chemistry, materials science, physics, and supercomputers are making it practical to consider first principles (de novo) predictions and simulations of the atomistic level physics and chemistry of complex systems and processes in the Chemical, Biological, and Materials Sciences. Our approach is to build a hierarchy of models each based on the results of more fundamental methods but coarsened to make practical the consideration of much larger length and time scales. Connecting this multi-paradigm multi-scale hierarchy back to quantum mechanics enables the application of first principles to the coarse levels essential for practical simulations of complex systems.

We will highlight some recent advances in multi-paradigm multi-scale methodology selected from: · The ReaxFF reactive force field for prediction of reactive processes in complex systems · The eFF method for electron dynamics of highly excited complex systems · PBE-lg and XYGI-OS quantum mechanics methods for accurate intermolecular interaction at modest cost · The 2PT method for fast accurate calculations of entropy from molecular dynamics that we will illustrate with recent applications to Energy, Catalysis, Nanotechnology, and Materials selected from:

Applications of Multiparadigm, Multiscale Methodologies to high velocity impact · EOS and phase transitions of materials from 2PT analysis of ReaxFF-lg reactive dynamics simulations · Spincoupling and superexchange in ferroelectrics · Mechanism of superconductivity in cuprates; strategies for increased Tc · Copper-Indium-Gallium-Selenide (CIGS)/CdS · Mechanisms of spin-coupling and superexchange in ferroelectrics · Hydration and hydrolysis processes in concrete (Ettringite) Functionalizing MOF, COF, ZIF Materials for cell catalysts including the oxygen reduction reaction · Solid acid, Solid oxide, alkaline, and ceramic electrolytes · Simulations of transport in dye synthesized photovoltaics including electrodes, ionic liquid, and reluctant · New anodes and electrolytes for Li batteries · ReaxFF-Monte Carlo methods for resolving partial occupations from Rietveld analyses into supercells with whole atoms; application to Mixed metal oxide catalysts for ammoxidation of propane

Characterization of Saharan dust from red rain precipitated over Athens, Greece

A. GODELITSA1*, P. NASTOS1, T.J. MERTZIMEKIS1, K. TOLI1, A. DOUVALIS2 AND R. SIMON3

1University of Athens, Greece
2University of Ioannina, Greece
3ANKA Synchrotron Facility, KIT, Germany

 Aeolian transport of Saharan dust influences significantly the rain acidity and furthermore the climate of the Mediterranean, causing among others, intense “red (or mud) rain” and even “red snow” episodes. During these episodes geological material from Sahara is deposited to the aquatic, terrestrial and urban environment [e.g. 1-3]. The Saharan dust samples were collected on membrane filters after intense “red rain” episodes over Athens megacity, Greece. Initial characterization by means of XRD, SEM-EDS and laser micro-Raman showed quartz, calcite and dolomite as major phases as well as phyllosilicates (mostly clays), rutile, zircon and goethite as minor constituents [4]. Preliminary analyses of metals using bulk XRF indicated Fe, Sr, Mn, Zn, Pb, Cr, Ni and Cu whereas gamma-ray spectroscopic measurements showed very low natural radioactivity and absence of human-produced nuclides. Detailed Synchrotron micro-XRF studies proved the presence of very hazardous elements, such as Pb and As, which had not been located on the samples by preliminary conventional investigation using SEM-EDS. It was also confirmed that many trace elements are intercorrelated (e.g. Fe-Mn-V-Cu) in other minor phases, of potential anthropogenic origin, hosted into the carbonate-silicate matrix. Subsequent Mössbauer spectroscopic study showed abundant Fe\(^{3+}\)-containing constituents and less Fe\(^{2+}\) phases. Moreover, sequential leaching experiments, using appropriate acids and ICP-MS analyses, revealed a high percentage of extractable Fe (and also Zn, Mn and Pb) due to carbonate phases comprising ~60% of the material. The above data can be important [see e.g. 5] for the geoavailability and bioavailability of aerosol-derived useful and harmful metals in southern Greece and generally in the entire semi-closed low-nutrient / low-chlorophyll marine ecosystem of eastern Mediterranean.

Isotope fractionation due to temperature gradients: Molecular dynamics simulation

Gaurav Goel1,2, Daniel J. Lacks2, James A. Van Orman1,2, Craig C. Lundstrom3, Charles E. Lesher4
1Department of Geological Sciences, Case Western Reserve University, Cleveland, OH 44106
2Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106
3Department of Geology, University of Illinois, Urbana, IL 61801
4Department of Geology, University of California, Davis, CA 95616

Experimental studies show that large isotope fractionation can occur along temperature gradients in silicate melts [1-3]. This thermally induced isotope fractionation can be much larger than the equilibrium fractionation between minerals and melts. In particular, lighter isotopes are found to be enriched in the hotter regions, and heavier isotopes are enriched in the colder regions of experimental charges, with the magnitude of the fractionation depending on the type of atom. The effect may be important in places such as at the edges of magma chambers and in other regions with sustained thermal gradients.

We have carried out molecular dynamics simulations to determine the factors that control the thermal fractionation of isotopes. The simulations are run for magnesium silicate melts (50-70% SiO2), with non-equilibrium molecular dynamics techniques used to produce the temperature gradient. The results of the simulations are in good agreement with experimental observations [e.g., 2, 3], both in terms of the absolute magnitude of the fractionation and the relative magnitudes for different types of atoms.

The simulations are carried out as a function of pressure, to predict the behavior under conditions deep inside the earth, which experiments have not yet addressed. Increasing pressure change the magnitude of the isotope fractionation per temperature change for atoms that form part of the network structure (Si, O), but its effects are insignificant for atoms that are not part of the network (Mg).


Pb and Zn distribution in stalagmites

J. Göttlicher1,*, S. Marks2, R. Simon1, R. Steininger1, A. Platte3, and S. Niggemann4
1Karlsruhe Institute of Technology, Institute for Synchrotron Radiation, Eggenstein-Leopoldshafen, Germany
(*correspondence: joerg.goettlicher@iss.fzk.de)
2Münster, Germany
3Letmathe, Germany
4Dechenhöhle, Letmathe, Germany

The impact of atmospheric emission on karst waters and karst bedrocks is investigated by analyzing speleothems (here: stalagmites of CaCO3) for metals that have been set free during the early years of industrialization. Letmathe in the Sauerland (one of the low mountain ranges in Germany) was chosen as a suitable area because two caves (Dechenhöhle and Hüttenbläser) are located in the main wind direction about 1 km away from a Pb and Zn smelter operating from 1862 to 1925. Additionally, slices from beech trees (∼155-165 y old) close to the cave were available for measuring their metal contents. Evidence for airborne Pb and Zn in this area came from analyses of gypsum encrustations at a nearby rock formation [1] and from deer antlers [2].

The young zone of the stalagmites is grey colored compared to the beige inner and therefore older part. X-ray fluorescence (XRF) spectra of the stalagmites measured at the SUL-X and FLUO beamline of the synchrotron radiation source ANKA show discrete peaks for Pb and Zn in the gray zone, highest contents at the boundary grey/beige and almost no Pb and Zn in beige zone. Pb and Zn are partly correlated. XRF spectra of beech trees exhibit a few spikes of Pb but they are not concentrated in the older part as expected. Zn is represented by a large number of peaks of different heights and frequencies with time. In both types of samples (stalagmite, wood) a discrete occurrence of Pb and Zn have been found rather than a homogeneous elevation during the time when atmospheric emission was most intensive. For the stalagmites the Pb and Zn pattern could be explained by particular entry or by enrichments at grain boundaries of crystallites which has to be proven. For the nature of metal distribution in trees no explanation has been found so far.

We thank ANKA for beamtime in the projects ENV-163 and ENV-186, and the forest officials of Letmathe for providing us slices of trees.

Plant impoundments as habitats for methanogenesis in tropical rainforest canopies

S. GOFFREDI1* AND W. USSLER III2
1Occidental College, Los Angeles, CA 90041, USA
(*correspondence: sgoffredi@oxy.edu)
2Monterey Bay Aquarium Research Institute, Moss Landing, CA 95039, USA (methane@mbari.org)

Tropical epiphytes within the family Bromeliaceae possess foliage arranged in compact rosettes capable of retaining water. This creates an unusual environment suspended in the rainforest canopy; acidic and anaerobic, with decomposition of impounded material. Archaeal communities within the tanks were dominated by methanogens (~90% of archaeal ribotypes) and community structure, although variable, was generally dominated by the hydrogenotrophic Methanoregula, with Methanocella, a specific clade of the acetoclastic Methanoseta, rice cluster II, and Methanosarcina also present. Close relatives were recovered previously from peat bog, acidic fens, and anoxic rice fields, all areas of similarly high organic content and low pH. All tanks (n = 63, comprised of 6 plant species, sampled over a two year period) showed presence of methanogens, as long as they exceeded ~22 cm in plant height or ~7 cm tank depth. Soil was negative for methanogens (n=8), except in one case, in which the dominant methanogen, related to Methanosarcina, was different from nearby bromeliads. Archaeal methyl coenzyme M reductase A copy numbers correlated with both plant height and light levels, suggesting that these environmental parameters affect conditions for methanogenesis. Methane-specific isotopes ranged from -45 to -63‰, and direct methane production rates, comparable to emissions measured for pasture and peat bogs, were measured in microcosm experiments. These results suggest that bromeliad-associated archaeal communities may play an important role in the cycling of carbon in tropical forests.

Osmium isotopic tracing of atmospheric emissions from an aluminum smelter

J. GOGOT*1, A. POIRIER1 AND A. BOULLEMANT2
1GEOTOP-UQAM, CP. 8888, Succ. Centre-ville, Montréal, Qc, Canada. H3C 3P8
(*correspondence: julien.gogot@gmail.com, poirier.andre@uqam.ca)
2RIO TINTO ALCAN, CRDA, 1955 bld Mellon CP 1250, Jonquiere (QC), G7S 4K8, Canada
(amiel.boullemant@riotinto.com)

In this study, we use osmium (Os) isotopes as a tracer of the environmental footprint of an aluminum smelter in Saguenay (Canada). This prebaked technology smelter transforms alumina (extracted from bauxite) in primary aluminum via carbon anodes. These latter are almost entirely consumed during the electrolytic process and are emitted as CO2 when reducing Al2O3 to Al(l). Such large gas emissions entrain inevitably some particulate matter (dust) at the stacks, despite gas and dust scrubbers demonstrate a more than 99.5% efficiency.

Heavy metals found in atmospheric emissions from this type of industry may have an isotopic composition significantly different from the local natural environment. The results of isotopic analysis of a sample of anode have revealed the presence of very radiogenic Os (187Os/188Os = 2.393 ± 0.005) compared to typical eroding continental crust (~1.2) and to usual anthropogenic sources (0.1-0.2). This suggested that Os might be a good candidate to follow a smelter’s environmental impact. The main objective of this study is to determine the isotopic composition of real emissions from an aluminum smelter for metals of geochemical interest (variable isotopic composition) and compare them with the natural surrounding environment.

During this meeting, we present Os results for a wide range of analyzed samples: carbonaceous material (anode); filters of emissions from the plant; samples of soils and sediment collected in the surrounding environment of the plant; and sedimentary sequence including pre-anthropogenic levels to characterize the natural background.
Insights into short-term changes in local and global seawater redox conditions during Cretaceous OAE 2

T. GOLDBERG1*, S.W. POULTON2, T. WAGNER2 AND M. REHKAMPER1

1Imperial College London, SW7 2AZ London, UK, (*correspondence: t.goldberg@imperial.ac.uk)
2Newcastle University, NE1 7RU, Newcastle upon Tyne, UK

The mid Cretaceous was a time of extreme greenhouse conditions. Related to this were a series of major black shale deposition events associated with global perturbations of the carbon cycle (ocean anoxic events; OAEs). These units potentially document periods of rapid climate change where the redox state of the Cretaceous ocean repeatedly fluctuated between oxic, anoxic and euxinic depositional conditions, linked to orbital-driven natural processes. Understanding these short-term cycles is essential for improving our knowledge of how future rapid climate warming may affect ocean chemistry.

Global seawater $\delta^{98/95}$Mo is reflected in euxinic environments, and differs accordingly to the extent of oxic and anoxic sinks [1]. To recognise short-term changes and relationships in the local, regional, and global redox state of seawater, high-resolution (millennial – centennial) Fe, S and redox sensitive trace elements (Mo, V, U, Cr) were paired with Mo isotopes ($\delta^{98/95}$Mo). The study site was a low latitude Palaeo-North Atlantic shelf region, deposited ~94 Ma ago.

In terms of local conditions, iron-sulphur systematics and biomarker evidence point to a predominantly sulphidic water column with short, periodic intervals of ferruginous conditions. Severe trace element depletion is mainly connected to sulphidic intervals, whereas ferruginous intervals show elemental recovery via continental input. A steady Mo isotopic composition is identified during local euxinia, indicating a reduction of the oceanic oxic sinks during OAE 2. During ferruginous conditions $\delta^{98/95}$Mo is affected by regional Mo uptake mechanisms. Conspicuous is an ~10-15 ky decrease in $\delta^{98/95}$Mo during euxinic deposition, coinciding with the peak of the positive carbon isotope excursion. This could be indicative of a massive increase in the spatial extent of ocean anoxia/euxinia in the Cretaceous oceans.


Clouds and the Faint Young Sun Paradox

COLIN GOLDBLATT1 AND KEVIN J. ZAHNLE2

1Astronomy Department, University of Washington, Seattle, WA 98195, USA (cgoldbla@uw.edu)
2Space Science and Astrobiology Division, NASA Ames Research Center, Moffett Field, CA 94035, USA (kevin.j.zahnle@nasa.gov)

We investigate the role which clouds could play in resolving the Faint Young Sun Paradox (FYSP). Lower solar luminosity in the past means that less energy was absorbed on Earth (a forcing of $-50\text{Wm}^{-2}$ during the late Archean), but geological evidence points to the Earth having been at least as warm as it is today, with only very occasional glaciations. We perform radiative calculations on a single global mean atmospheric column. We select a nominal set of three layered, randomly overlapping clouds, which are both consistent with observed cloud climatologies and reproduced the observed global mean energy budget of Earth. By varying the fraction, thickness, height and particle size of these clouds we conduct a wide exploration of how changed clouds could affect climate, thus constraining how clouds could contribute to resolving the FYSP. Low clouds reflect sunlight but have little greenhouse effect. Removing them entirely gives a forcing of $+25\text{Wm}^{-2}$ whilst more modest reduction in their efficacy gives a forcing of $+10$ to $+15\text{Wm}^{-2}$. For high clouds, the greenhouse effect dominates. It is possible to generate $+50\text{Wm}^{-2}$ forcing from enhancing these, but this requires making them 3.5 times thicker and 14K colder than the standard high cloud in our nominal set and expanding their coverage to 100% of the sky. Such changes are not credible. More plausible changes would generate no more than $+15\text{Wm}^{-2}$ forcing. Thus neither fewer low clouds nor more high clouds an provide enough forcing to resolve the FYSP. Decreased surface albedo can contribute no more than $+5\text{Wm}^{-2}$ forcing. Some models which have been applied to the FYSP do not include clouds at all. These overestimate the forcing due to increased CO$_2$ by 20 to 25% when $p\text{CO}_2$ is 0.01 to 0.1 bar [1, 2].

Scaling of critical zone processes in the Prairie Pothole region, USA

MARTIN GOLDHABER1, CHRISTOPHER MILLS, JEAN MORRISON AND CRAIG STRICKER

1USGS, Denver, CO, USA, (*correspondence; mgold@usgs.gov, cmills@usgs.gov, jmorrison@usgs.gov, cstricker@usgs.gov)

The Prairie Pothole Region, which occupies 750,000 km² of the north central U.S. and south central Canada is one of the most important ecosystems in North America. It contains millions of small wetlands underlain by glacial till that are internally drained within discrete, km-scale basins. We studied the geochemistry of soils, sediments, wetland water, and groundwater in the 92 hectare Cottonwood Lakes (CWL) area of North Dakota. The CWL area includes upland groundwater recharge wetlands with compositions similar to rainwater (TDS 150 mg/l), and a discharge wetland at a local topographic low only 200m from the recharge wetlands. Oxygenated water interacting with pyrite in surficial glacial till has oxidized the till to depths >10 m. Coupled fluid flow and chemical reaction modeling shows that this oxidation process has taken >10³ years. The resulting SO₄²⁻-enriched fluids have migrated from upland recharge areas and accumulated in the discharge wetland which has >2500 mg/l SO₄²⁻. The drastic variability in recharge and discharge wetland chemistry is reflected by fauna and flora. Sulfur isotope data support the conclusion that isotopically light pyrite, origionally from marine shale (mean δ³⁴SSO₄ =-16‰) is the source of groundwater sulfate (δ³⁴SSO₄=-7.5 to -15.9‰). Heavier δ³⁴SSO₄ values within discharge wetlands (maximum +4‰) is evidence that bacteria are reducing SO₄²⁻ to sulfide, a process that drives the precipitation of high Mg calcite.

Our evaluation of literature data on water compositions of 178 wetlands throughout a 10³ km² area surrounding the study site document that oxidation of pyrite and formation of SO₄²⁻ enriched wetlands has occurred over a large area in North Dakota.

Oxygen isotope variations in the Allende CV3 meteorite

A. GOLDMANN1,2, A. PACK2, M. GELLISSEN3, N. ALBRECHT2, J. ZIPFEL4 AND H. PALME4

1Leibniz-Universität Hannover; 2Georg-August-Universität Göttingen; 3Christian-Albrechts-Universität Kiel; 4Senckenberg Forschungsinstitut und Naturmuseum, Frankfurt

Introduction

The Allende (CV3) carbonaceous chondrite consists of mm-sized chondrules, fine-grained matrix, Ca- and Al-rich inclusions (CAIs), dark inclusions (DI) and amoeboid olivine aggregates (AOA). Various components of the Allende meteorite fall on a mixing line in the δ¹⁷O vs. δ¹⁸O space [1]. In this study, we investigate isotope variations of small bulk samples (~0.3 – 1.1 g) and compare the variations with chemical data of the same aliquots.

Samples and Measurement techniques

37 of 39 samples of a 22.5 mm² large and 4 mm thick slice of the meteorite were analyzed. One sample (C4) contained a macroscopically visibly CAI, one (F3) a large DI. Oxygen isotopes were analyzed in Göttingen using IR laser fluorination in combination with GC-irmMS using a MAT 253 gas source mass spectrometer. The Δ¹⁷O is calculated relative to the rocks- and minerals-defined TFL (N > 700) with a slope of β = 0.5151±0.0007 (1σ) and an intercept of γ = -0.0014±0.008 (1σ). The accuracy and precision of a single isotope analysis is ~0.15 ‰ and ±0.04 ‰ in δ¹⁷O.

The chemical analyses were obtained by XRF in Cologne.

Results

The O-isotope data fall on the AML. The Δ¹⁷O_TFL shows a spread from -4.6 ‰ to -2.3 ‰. The lower limit is marked by sample C4 (CAI) and the upper limit by the DI in sample F3. Excluding these 2 samples, a spread in Δ¹⁷O of -4.1 to -3.0 ‰ is observed. For the remainig samples, no correlation between chemical composition (e.g. Al content) and Δ¹⁷O is observed. The Al₂O₃ concentrations range from 2.6 – 4.3 wt.%, with constant Ca/Al-ratios..

Discussion

A correlation between Δ¹⁷O and chemistry is expected if variations in Al (and other refractory elements) is caused by addition of CAI-like material. Such a correlation is not observed. This suggests the existence of an oxygen component, independent of the chemical variability. Implications with respect of the correlation between O- and Cr-isotopes [3] will be discussed.

Nanoparticles of X-ray amorphous mineralogical substances

YE.A. GOLUBEV
Institute of Geology, Syktyvkar, 167982, Russia
(golubev@geo.komisc.ru)

Representations about the particular ultradisperse structural state of x-ray amorphous mineralogical substances (mineraloids), distinct from atomic-molecular are developed [1-4]. For mineraloids it are find out and in details described submicro-nanoscale structures of natural solid bitumens, fossil resins, of some inorganic metacolloids by HRTEM, STM, AFM, SEM. This has allowed revealing various species of superstructural orderings in mineraloids, to define its mechanisms, to allocate key value of influence of the heating factor for the sizes nanoparticles in organic mineraloids.

Results of studying submicro-nanoscale structures and mechanisms of their ordering are important for modifying technological properties of natural substances, making of geomaterials. Special interest cause mineraloids with periodically-ordered nanoscale structures like noble opal has aroused. The similar regular structures are characteristic for a row organic and inorganic mineraloids.


Statistical evaluation of the Holocene climate parameters in the NE of European Russia (from palynological data)

YU.V. GOLUBEVA* AND YE.A. GOLUBEV
Institute of Geology, Komi Science Centre, Ural Division of RAS, 167982 Syktyvkar, Russia, (*correspondence: bratushecak@geo.komisc.ru)

In the given work present paleoclimatic investigation included palynological and statistical analyses, radiocarbon dating of the Holocene lake, alluvial (oxbow lake) and swamp sediments in middle and northern taiga subzones of the Komi Republic. On the basis of cores of four boreholes and fourteen outcrops, synchronous spectra correlation and Holocene separation were accomplished [1].

Mean annual and July temperatures were estimated by zonal method of the Holocene palaeoclimates reconstruction [2], based on palynological assemblages for characteristics of environmental changes during the interval. It has been established that the sediments accumulated during the Preboreal–Subatlantic interval, when repeated climatic changes occurred.

To determine the main trends of paleoclimate changes climatic curves have been drawn. The curves show deviations of the mean annual and July temperatures during the Holocene from their current values. For this purpose, the statistical weight of mean temperature values are taken into account in paleoclimatic curves approximating, as the temperature ranges in certain intervals of the Holocene vary considerably.

According to the palynological data and statistical analyses three periods with warmer climatic conditions (Early Boreal, Middle Subboreal and Late Atlantic) were estimated. It is established, that climatic optimum have developed at the end of the Atlantic period to what distribution of the most thermophilic tree species (oak, elm, hazel and maple) and the highest temperatures testifies. The Atlantic period is characterized by mean July temperature on 2.5–3.5 °C and mean annual temperature on 2–3 °C warmer, than at the present time. The Boreal and Subboreal temperature maxima had the subordinated value. Thus, from the Preboreal period the increase tendency of temperatures up to the maximal values at the end of the Atlantic period is observed. Then reduction of temperatures to the present has followed.

This research was supported by grant by the Program of Presidium RAS n. 14.

Stability of Cu adsorbed onto clay surfaces: An experimental and computational study

MÁRIO A. GONÇALVES¹, DAVID MARTINS¹ AND STEPHEN C. PARKER²

¹Departamento de Geologia and CREMINER/LA-ISR, Faculdade de Ciências U. Lisboa, Lisboa, Portugal (mgoncalves@fc.ul.pt, dmmartins@fc.ul.pt)
²Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom (s.c.parker@bath.ac.uk)

The stability of adsorbed metals onto mineral surfaces is an essential property in controlling their ultimate fate in the environment. This study addresses this problem with the analysis of batch and flow-through (kinetic) experiments using Cu and illite, complemented with ab-initio and molecular dynamics studies. Experiments were performed at pH 4.5 to 6.5, and 10⁻⁴ M – 10⁻³ M ionic strength.

Batch and kinetic experiments gave consistent results on total adsorbed Cu per gram of adsorbent: 6.4 – 9.1 x 10⁻⁵ mol/g for pH 4.5, and 9.0 – 13.0 x 10⁻⁵ mol/g for pH 5.5. Results follow a Langmuir-type adsorption isotherm, but at pH 6.5 surface Cu precipitation occurs.

Desorption rates were measured with the results from flow-through experiments, and ranged between 1.0 – 2.4 x 10⁻¹⁰ mol/m²/min. The amount of desorbed Cu ranged between 6 and 54% of the total adsorbed Cu. These results indicate that Cu surface stability is favoured for high pH/low ionic strength solutions, also lending support on the Eigen- Wilkins-Werner mechanism [1]. Metal adsorption on edge surface sites of clays is shown by spectroscopic studies [2].

We are also investigating the edge surface sites further by calculating the different modes of adsorption of Cu complexes at edge sites and comparing them to adsorption on (001) surface using atomistic simulation techniques. Initially, the static simulation code METADISE [3] was used to explore the structure and the stability of the different surface cuts for the (010), (100), and (-110) edge surfaces of an idealised pyrophyllite structure. Inner and outer-sphere Cu complexes are currently being optimised using DFT within the VASP code [4] to aid in the interpretation of the experimental results.

Contribution of Project KADR Waste PTDC/CTE-GEX/82678/2006 funded by FCT (Portugal).

Redox state of lithospheric mantle in central Siberian craton: A Mössbauer study of peridotite xenoliths from the Udachnaya kimberlite

A.G. GONCHAROV¹,², D.A. IONOV², L.-S. DOUCET² AND I.V. ASHCHEPKOV³

¹IPGG RAS, Saint-Petersburg, Russia ( correspondence: ag.goncharov@ipgg.ru)
²Université J. Monnet, Saint-Etienne 42023, France
³Inst. Geology & Mineralogy, Novosibirsk 630090, Russia

Redox state in a vertical profile of lithospheric mantle in central Siberian craton (Russia) was determined based on peridotite xenoliths from the 360 My old Udachnaya kimberlite. Equilibration temperatures (T) and pressures (P) for garnet peridotites are 860-1340°C [1]; P values for spinel peridotites were estimated from T (760-965°C) projections to a conductive geotherm defined by the garnet peridotites. Mössbauer spectroscopy was used to obtain Fe³⁺/ΣFe ratios in garnet from 15 samples (9–23%) and spinel from 7 samples (6-22%). Oxygen fugacity (fO₂) was calculated using oxygen thermobarometry. The fO₂ decreases with pressure, hence depth. Low-T samples (750-1000°C; P = 2.6-5.3 GPa) yield fO₂ (ΔFMQ) = (0.0) to (-1.8) log units whereas high-T (1200-1350°C; 5.4-6.8 GPa) samples have fO₂ (ΔFMQ) = (-2.4) to (-3.1) log units. The low-T peridotites overlap the graphite and carbonate stability fields; the high-T garnet peridotites plot in the diamond stability field. Speciation of hypothetical C-O-H fluids coexisting with the rocks was assessed from the T, P and fO₂ data. Fluids for the high-T, hence the deepest, samples mainly consist of methane and water indicating that these “craton roots” are not likely to contain partial melts because of high T’s of peridotite solidus in the presence of reduced C-H compounds.

Influence of thiol-containing ligands for the aggregation and dissolution of metallic silver nanomaterials

ANDREAS P. GONDIKAS1, BRIAN REINSCH2, GREG LOWRY2 AND HEILEEN HSU-KIM*1

1Duke University, Civil and Env. Eng., Durham, NC, USA
(*correspondence: hsukim@duke.edu)
2Carnegie Mellon University, Civil and Env. Eng., PA, USA

The environmental fate and mobility of metallic nanoparticles (NPs) in natural waters will be strongly influenced by reactions between the particle surfaces and metal-binding organic ligands that are prevalent in natural waters. Thiol-containing organics are known to dominate the speciation of soft-sphere metals such as ionic silver (Ag⁺) in the environment [1]. Furthermore, the type and reactivity of the synthetic coating that is used during the synthesis of the nanomaterials will be a key factor controlling interactions with thiol-containing organic ligands. The objective of this work was to examine how thiols can modify particle surfaces and their reactivity during aggregation and dissolution of the nanoparticles. We studied zero valent silver (Ag) NPs with two types of coatings: citrate (CIT) and polyvinylpyrrolidone (PVP). Our studies involved cysteine (CYS) and N-acetyl-cysteine (NAC), two low molecular weight thiol ligands that we utilized as analogues for the natural organics that are expected to bind dissolved Ag⁺ in the aquatic environment.

Aggregation and dissolution experiments with CIT- and PVP-coated Ag NPs demonstrated that thiol-containing ligands increased aggregation rates of the particles, depending on solution ionic strength and type of thiol. The increase in aggregation was greater for the PVP-coated Ag NPs relative to the CIT-coated NPs. The addition of cysteine to Ag NP suspensions also increased the dissolved Ag concentration. These results indicated that cysteine was simultaneously sorbing to the Ag NPs and promoting their dissolution, resulting in surface modifications that increased aggregation rates. These results were supported by silver L-III-edge and sulfur K-edge X-ray absorption spectroscopy measurements that showed oxidation of the silver and the formation of Ag(+I)-CYS bonds for Ag NPs that were exposed to CYS.

Overall, our study highlights the importance of the coating and Ag⁺-binding organic ligands for modifying the surface of silver nanomaterials in environmental settings. Sorption of natural organics alters the aggregation and solubility of the nanomaterials, and ultimately, will influence their persistence in the environment.

Mantle-to-surface magma dynamics at Mauna Loa and Kīlauea, Hawai’i

H.M. GONNERMANN1*, M. POLAND2, J.H. FOSTER3, B. BROOKS3, C.J. WOLFE3,4 AND A. MIKLIUS2

1Department of Earth Science, Rice University, Houston, TX 77005 (*correspondence: helge@rice.edu)
2U.S. Geological Survey, Hawai’ian Volcano Observatory, Hawai’i National Park, HI 96718
3Department of Geology and Geophysics, SOEST, University of Hawai’i, Honolulu, HI 96822
3Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC 20015

In 2002 Mauna Loa Volcano, Hawai’i, began a nearly decade long period of inflation. Almost simultaneously, inflation and heightened activity occurred at neighboring Kīlauea Volcano. We address the question if and how both volcanoes are dynamically linked.

We model asthenospheric and crustal magma flow and pressure using a numerical model that integrates kinematic models of volcano deformation with a lumped parameter flow model. The model is constrainted by continuous global position system (GPS) measurements of deformation at both volcanoes. The past decade of summit deformation at Kīlauea and at Mauna Loa can both be explained by coupling crustal magma flow and storage to a common permeable asthenospheric melt zone beneath both volcanoes. Each volcano’s shallow crustal magma system is connected to the asthenospheric melt zone by a lithospheric magma plumbing system through which changes in magma pressure can be transmitted. Consequently, pore pressure diffusion within the porous zone produces a dynamical linkage between both volcanoes and increased activity at one volcano may or may not be correlated with activity at its neighbor, depending on the interplay between deep and shallow magmatic processes.

A characteristic pore pressure diffusion time between both volcanoes of approximately ½ year explains the time-delayed onset of inflation at Mauna Loa relative to Kīlauea during 2002. Moreover, magma flow paths within the asthenospheric melt zone capture compositionally distinct magma from different parts of the asthenospheric melt source over long periods of time, consistent with geochemical observations. Because the time required for melt flow within the porous layer between both volcanoes is about three orders of magnitude slower than pore pressure diffusion. Consequently, significant redistribution of melt by porous flow requires time scales of 100s to 1,000s of years, so that decadal changes in surface activity are unlikely to affect long-term trends in magma geochemistry.

Oxidation of Fe(II) in natural waters at high nutrient concentration

ARIDANE G. GONZÁLEZ, J. MAGDALENA SANTANA-CASIANO*, NORMA PÉREZ AND MELCHOR GONZÁLEZ-DÁVILA

Departamento de Química, Facultad de Ciencias del Mar, Universidad de Las Palmas de Gran Canaria, Campus de Tafira, 35017 Las Palmas, Spain

The Fe(II) oxidation kinetic was studied in seawater enriched with nutrients as a function of pH (7.2-8.2), temperature (5-35°C) and salinity (10-36.72) and compared with seawater media. The effect of nitrate (0-1.77·10⁻³ M), phosphate (0-5.80·10⁻⁵ M) and silicate (0-2.84·10⁻⁴ M) was studied at pH 8.0 and 25°C. The Fe(II) oxidation is faster when a high nutrient concentration is present, decreasing the t₁/₂ and compromising the permanence of Fe(II) in nutrient rich waters. The most important nutrient affecting the oxidation rate is silicate. A kinetic model was applied to the experimental results in order to follow the speciation of each Fe(II) species and to compute the fractional contribution to the overall rate constant as a function of pH. The speciation was controlled by Fe²⁺ from pH 6 to 7.9 and FeCl⁺ from pH 6 to 7.6. FeH₃SiO₄⁺ was the most important species for pH higher than 7.6, when the concentration of total silicate was 1.41·10⁻⁴ M. The Fe(OH)⁺ controlled the kinetic process at pH lower than 8.1, while the Fe(OH)₂ began to control the oxidation rate constant at higher pH values.
Microbial induced mineralization in Co-rich ferromanganese crusts from the Scotia Sea

F.J. GONZÁLEZ1*, L. SOMOZA1, A. MALDONADO2, T. TORRES3 AND J.E. ORTIZ3

1Geological Survey of Spain (IGME). Madrid, Spain
(*correspondence: fj.gonzalez@igme.es)
2Inst. Andaluz Ciencias Tierra, (IACT: CSIC/UG). Spain
3Lab. Estratigrafía Biomolecular (LEB/UPM). Madrid, Spain

Co-rich ferromanganese crusts were collected at 2000-2500 m water depth in oceanic ridges and seamounts from the Scotia Sea during the SCAN-2004 and SCAN-2008 oceanographic cruises. Fe-Mn crusts form botryoidally pavements up to 50 mm thick on tholeiitic oceanic basalts. According to data of X-ray diffraction and petrographic observations the crusts are essentially composed by poorly crystalline feruginous-vernadite (δ-MnO2), and goethite and detrital quartz and phyllosilicates as accessory minerals. The Mn/Fe ratio in bulk samples is 1.1, indicating precipitation from cold ambient of seawater onto hard rock substrates. All the studied Fe-Mn crusts concentrate strategic elements (Co, Ni, Tl, REE or PGE) several orders of magnitude above the mean concentration in the Earth’s crust.

Fe-Mn crusts occur as fine laminated manganese oxides structures. SEM imagings reveal abundant like-microbe tubular sheaths (less than 1 µm in diameter and 10-200 µm long). These textural features can be due to the Mn-biomineralization action of chemolithoautotrophic microorganisms (Leptothrix spp., Metallogenium?). We interpret these filaments as fossilised bacteria (mineralised biofilms) according to their morphology, size ranges and textural features of colonial associations, similar to modern bacteria. They could be easily formed by action of Mn-oxidizing bacteria forming sheaths stained by vernadite, precipitated within extracellular structures. EDX-SEM and Electron Microprobe analyses show the chemical composition of fossilised bacterial biofilms with enrichments in strategic elements with respect to the bulk sample: 22.6% Mn, 22.4% Fe, 1.6% Ti or 1.5% Co and also 7.6% C and 6.8% F. Biomarkers like n-alkanes (n-C18) and nitrogen compounds, detected by GC-MS analysis, could be related to the bacterial mineralization. These findings suggest a link between the microbial and the mineralization. The microbes could have played a critical role in the accumulation of metals through sorptive, catalytic and oxidative processes forming Fe-Mn crust deposits with economic potential. It also remarks the high scavenging efficiency of vernadite for remediation or recovery of trace metal contamination.

Arsenic biomineral formation leads to partial encrustation of thermoacidophilic archaea

P. GONZALEZ*, J. WEIJMA AND C.J.N. BUISMAN

Wageningen University, Sub-dept. of Environmental Technology. Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands. P.O. Box 17, 6700 AA Wageningen (*correspondence: paulaa.gonzalezcontreras@wur.nl)

Acidophilic iron oxidizing Sulfolobales spp. mediate the formation of jarosite nanoprecipitates and bioscorodite precursors [1]. In batch experiments, scorodite biomineral formation by Sulfolobales spp. was induced at a pH of 1 and 75°C [2]. At these conditions, we observed formation of precursors (nuclei) of scorodite on the cell surface. This suggests that the mechanism of scorodite formation begins with the sorption of ferric iron and arsenate onto the cell surface, followed by the formation of ferric arsenate nuclei from the adsorbed metal species. By growth of the nuclei and ageing of the precipitates, scorodite crystals were formed on the cell surface, which led to a partial encrustation of the cells. In the absence of arsenic, jarosite precipitates were found on the cell surface, but this did not result in encrustation.

Figure 1. SEM photograph of the biominalized scorodite by Sulfolobales. Photograph with 30000 magnification and SE detection at 3.5 KV.

Weathering intensity in the Mesoproterozoic and modern large-river systems: A comparative study in the Belt-Purcell supergroup

I. GONZÁLEZ-ÁLVAREZ1,2* AND R. KERRICH2
1CSIRO, Australian Resources Research Centre, Earth Science and Resource Engineering, Kensington, WA 6151, Australia.
2Department of Geological Sciences, The University of Saskatchewan, 114 Science Place, Saskatoon SK, S7N 5E2

River systems are the main contributors of continental siliciclastic sediments to ocean basins, and potentially preserve a record of weathering conditions across the catchment areas. Proterozoic rivers have been viewed as mostly braided systems due to the lack of influence of rooted vegetation that produces fast channel lateral migration, high run-off rates, and low bank stability. Many large-scale vegetation that produces fast channel lateral migration, high channel incision, and hig°CIA values throughout the succession (BPS).

BPS CIA values of 70 are commensurate with modern humid-dry tropical conditions in modern rivers such as the Orinoco, Parana, Mekong and Amazon rivers, with arid-template climate period in between. This study evaluates secular weathering variations for the Mesoproterozoic based on the Chemical Index of Alteration (CIA), accounting for post-depositional K addition and specifically for siliciclastic units of the Belt-Purcell Supergroup (BPS). BPS CIA values throughout the succession span 60-85, averaging ~70. These values could be linked to CO₂ emissions from magmatism accompanying rifting of Columbia at ~1.4 Ga. The new data, along with K-corrected CIA data from the literature, could be interpreted as recording a rising trend from ~50 at ~2.5 Ga to ~75 at 1.6 Ga, a low of 50 at ~1.5 Ga, and ~50-60 from 1.4 Ga to 1.0 Ga. However, CIA link to global geodynamic events remains challenging due to scarcity and lack of space-time resolution of data sets.

BPS CIA values of ~70, are commensurate with modern large river systems such as the Orinoco, Nile and Amazon rivers. The Appekunny and Grinnell formations (Lower BPS succession) display two intense weathering periods (~80±5) equivalent to humid-dry tropical conditions in modern rivers such as the Orinoco, Parana, Mekong and Amazon rivers, with a arid-template climate period in between.

This study suggests that BPS CIA values reflect a more aggressive chemical weathering, since Proterozoic rivers had less sediment residence time due to lack of vegetation cover, and therefore, faster transport time than their modern counterparts. To achieve high CIA values in shorter periods of time without vegetation cover, higher chemical weathering conditions need to be invoked.

Geodynamic implications of >1 Ga Re-Os model ages in PGM from the Dobromiritsi Ultramafic Massif, Central Rhodope, Bulgaria

J.M. GONZÁLEZ-JIMÉNEZ1 W.L. GRIFFIN1, F. GERVILLA2, T. KERESTEDJIAN3, S.Y O’REILLY1 AND N.J. PEARSON1
1GEMOC ARC National Key Centre, Sydney, Australia.
2Dpt. Mineralogy & Petrology, University of Granada, Spain.
3Geological Institute, Bulgarian Academy of Sciences, Bulgaria. (jose.gonzalez@mq.edu.au.; bill.griffin@mq.edu.au; sue.oreilly@mq.edu.au; npearson@mq.edu.au).

The Dobromiritsi Ultramafic Massif is a relic of meta-ophiolitic mantle, located in the Central Rhodope Dome in southern Bulgaria. The ultramafics have been trust over Paleozoic (470-450 Ma; [3]) para-gneisses and are unconformably covered by Tertiary volcano-sedimentary rocks. The massif consists of strongly metamorphosed (greenschist to amphibolite facies) harzburgite and dunite, containing several chromitite pods, and cross cut by pyroxenite veins [2]. Os-rich laurite (Ru,Os)S2 ± Os-Ir alloys ± pentlandite constitute the PGM assemblage in unaltered chromite. In altered zones, Os-poor partially desulfurized laurite, sometimes replaced by Ru-rich base-metal sulfides + Os-Ir alloys is the common assemblage [1].

In situ Re-Os analyses reveal that unaltered laurite has a small spread in TRD (300-600 Ma). In contrast, 11 out of 36 of the altered grains yield TMA (and TRD) model ages > 1 Ga and up to 2.2 Ga (187Os/188Os = 0.1124- 0.1206; average = 0.1173 ± 0.003; 2σ). These unradiogenic Os signatures require a mantle source that underwent differentiation processes in the Proterozoic; we suggest that this source lies in the upper mantle source that underwent differentiation processes in the Proterozoic; we suggest that this source lies in the ultramafic mantle, located in the Central Rhodope Dome in southern Bulgaria. The ultramafics have beentrust over Paleozoic (470-450 Ma; [3]) para-gneisses and are unconformably covered by Tertiary volcano-sedimentary rocks. The massif consists of strongly metamorphosed (greenschist to amphibolite facies) harzburgite and dunite, containing several chromitite pods, and cross cut by pyroxenite veins [2]. Os-rich laurite (Ru,Os)S2 ± Os-Ir alloys ± pentlandite constitute the PGM assemblage in unaltered chromite. In altered zones, Os-poor partially desulfurized laurite, sometimes replaced by Ru-rich base-metal sulfides + Os-Ir alloys is the common assemblage [1].

In situ Re-Os analyses reveal that unaltered laurite has a small spread in TRD (300-600 Ma). In contrast, 11 out of 36 of the altered grains yield TMA (and TRD) model ages > 1 Ga and up to 2.2 Ga (187Os/188Os = 0.1124- 0.1206; average = 0.1173 ± 0.003; 2σ). These unradiogenic Os signatures require a mantle source that underwent differentiation processes in the Proterozoic; we suggest that this source lies in the ultramafic mantle, located in the Central Rhodope Dome in southern Bulgaria. The ultramafics have beentrust over Paleozoic (470-450 Ma; [3]) para-gneisses and are unconformably covered by Tertiary volcano-sedimentary rocks. The massif consists of strongly metamorphosed (greenschist to amphibolite facies) harzburgite and dunite, containing several chromitite pods, and cross cut by pyroxenite veins [2]. Os-rich laurite (Ru,Os)S2 ± Os-Ir alloys ± pentlandite constitute the PGM assemblage in unaltered chromite. In altered zones, Os-poor partially desulfurized laurite, sometimes replaced by Ru-rich base-metal sulfides + Os-Ir alloys is the common assemblage [1].

In situ Re-Os analyses reveal that unaltered laurite has a small spread in TRD (300-600 Ma). In contrast, 11 out of 36 of the altered grains yield TMA (and TRD) model ages > 1 Ga and up to 2.2 Ga (187Os/188Os = 0.1124- 0.1206; average = 0.1173 ± 0.003; 2σ). These unradiogenic Os signatures require a mantle source that underwent differentiation processes in the Proterozoic; we suggest that this source lies in the ultramafic mantle, located in the Central Rhodope Dome in southern Bulgaria. The ultramafics have beentrust over Paleozoic (470-450 Ma; [3]) para-gneisses and are unconformably covered by Tertiary volcano-sedimentary rocks. The massif consists of strongly metamorphosed (greenschist to amphibolite facies) harzburgite and dunite, containing several chromitite pods, and cross cut by pyroxenite veins [2].
Multiphase magmatic history of the Oman-UAE ophiolite

K.M. GOODENOUGH1*, M.T. STYLES2, R.J. THOMAS2, D.I. SCHOFIELD3, Q.G. CROWLEY4 AND I.L. MILLAR2

1British Geological Survey (BGS), West Mains Road, Edinburgh EH9 3LA (*correspondence: kmgo@bgs.ac.uk)
2BGS, Keyworth, Nottingham, NG12 5GG
3BGS, Columbus House, Tongwynlais, Cardiff, CF15 7NE
4Dept. Of Geology, Trinity College, Dublin 2, Ireland

The Oman-United Arab Emirates (UAE) ophiolite is the largest ophiolite complex in the world. The majority of the ophiolite lies in Oman, but it has a northerly extension into the UAE. This has been mapped and studied in detail by the BGS since 2002, funded by the UAE’s Ministry of Energy.

The Oman-UAE ophiolite was traditionally interpreted as a classic mid ocean-ridge ophiolite, but more recently it has been recognised that a second, voluminous phase of magmatism is superimposed upon the early MORB-like ophiolite sequence. In the UAE, our field mapping has shown that this later magmatic phase forms extensive intrusions including large gabbro plutons, tonalite bodies and mafic dyke swarms throughout the crustal sequence and the mantle transition zone. The later magmatism has been dated at 96.4 to 95.2 Ma [1], coeval with similar magmatism in the Oman sector of the ophiolite [2]. The age of the early magmatism is not yet known.

Petrology and mineralogy of the early magmatic phase are consistent with formation at a spreading ridge, but the magmas of the later phase were more hydrous. Dykes and lavas from the early magmatic phase have MORB-like geochemistry, whereas those from the later magmatic phase show geochemical features of subduction-related magmatism, such as lower Ti/V and Zr/Y. Whole-rock Pb isotope data also distinguish the two phases, and support a supra-subduction zone setting for the later phase.

The youngest, volumetrically minor magmatism, recorded in the UAE sector of the ophiolite as localised mafic dykes, has geochemical and isotopic signatures more like those of ocean island basalts, and may be associated with an extensional, post-obduction event. This magmatism is tentatively dated at about 91 Ma.


Vadose zone controls on weathering intensity and depth: Observations from granitic and basaltic saprolites

B.W. GOODFELLOW1*, G.E. HILLEY1, O.A. CHADWICK2, M.S. SCHULZ3 AND E. SHELEF2

1Department of Geological and Environmental Sciences, 450 Serra Mall, Stanford University, Stanford, CA 94131, USA. (hilley@stanford.edu; shelef@stanford.edu; *correspondence: bgood@stanford.edu)
2Department of Geography, University of California Santa Barbara, CA 93106, USA (oac@geog.ucsb.edu)
3US Geological Survey, 345 Middlefield Rd. MS-420, Menlo Park, CA 94025, USA (mschulz@usgs.gov)

An investigation of vadose zone weathering processes has been undertaken on saprolites developed in Californian granitoids and Hawaiian basalts. Granitoid observations have been made across a drying gradient (declining precipitation, increasing temperature), from the coast inland to the Sierra Nevada foothills. Observations of basalt weathering have been made across strong precipitation/hydrological gradients on Kauai and Hawaii and along a chronosequence of weathering profiles developed on lava flows ranging from ~10–40 ka on Hawaii to >4 Ma on Kauai.

Results indicate strong climatic control, through infiltration, on the depth and intensity of weathering in both lithologies. Dry, lower infiltration sites display only thin saprolites, strongly influenced by rock texture. At wet, higher infiltration sites, the vadose zone is comprehensively altered to saprock and saprolite. In both granitoids and basalt, vadose zone and weathering depth appear to be governed by local base level. This is demonstrated by weathering to just above sea level, sharp contrasts between unweathered bedrock in perennial streams and weathered rock on adjacent slopes, and the presence of deep saprolites on steep slopes.

In addition, laboratory analyses of granitoids indicate that vadose zone hydrology exerts a fundamental control on the effective operation and relative dominance of the key weathering reactions. In zones of matrix permeability, oxidation of Fe-bearing phases comprehensively disaggregates the rock but results in minor mass loss and clay mineral formation. Conversely, the higher transient flow rates that characterize zones of fracture permeability result in plagioclase hydrolisis, significant mass losses and accompanying clay mineral formation. A variable hydrological regime may also contribute to high partial pressures of O2 in vadose zone pore waters and pore spaces, thereby enhancing the oxidative environment and predisposing grussic saprolite formation in granitoids.
**Mn/Cr systematics in carbonaceous chondrites: Mineral isochrons versus stepwise dissolution**

C. Göpel1*, J.-L. Birck1 AND B. Zanda2

1IPGP- Géochimie et Cosmochimie, 1 Rue Jussieu, 75238 Paris Cedex 05, France (*correspondence: gopel@ipgp.fr)
2MNHN & CNRS, 61 rue Buffon, 75005 Paris, France

The Mn/Cr isotope systematics of meteorites holds a double information: the $^{53}\text{Cr}/^{53}\text{Mn}$ system may be used for dating while $^{53}\text{Cr}$ isotope systematics yields information on the mixing of nucleosynthetically distinct components of the solar system. We present Mn/Cr data on two recently discovered carbonaceous meteorites. Sequential dissolution steps of bulk rock powder were performed but also for the first time for carbonaceous meteorites the Mn/Cr systematics were measured on separated minerals.

Tafassasset is equilibrated and recrystallized. Its minerals are metal, olivine, low Ca pyroxene, feldspar with accessory chromite and phosphate. Tafassasset’s classification as a CR chondrite or a primitive achondrite is still debated [1, 2]. Chromite, olivine and bulk rock define an isochron whose slope corresponds to $\frac{\Delta^{53}\text{Mn}}{\Delta^{53}\text{Cr}} = 3.07 \times 10^{-6}$ and $\varepsilon^{53}\text{Cr} = 0.07$ translating into an absolute age of 4563.4 ± 0.4 x10^6 y using the LEW Cliff 86010 anchor [3]. With the exception of the first leaching step, all dissolution steps fall on a linear array. The age obtained by this procedure, 4563.6 ± 1.3 x10^6y based on the LEW Cliff 86010 anchor [3]. All mineral fractions as well as the bulk rock of Paris exhibit a positive $^{54}\text{Cr}$ anomaly. In contrast, the sequential dissolution pattern is similar to that of Murchison.

Paris is the less altered CM chondrite known to date with affinities to CO chondrites. It contains more chondrules, refractory inclusions and metal but less matrix than the others. Forsterite, fayalite, a separate of fine-grained material attached to chondrules (presumably FGR) and an aliquot of the bulk rock were analyzed for Mn/Cr systematics. All samples fall on a line with a slope of $\frac{\Delta^{53}\text{Mn}}{\Delta^{53}\text{Cr}} = 0.179$. This slope corresponds to an age of 4566.54 ± 0.55 x10^6 y based on the LEW Cliff 86010 anchor [3]. All mineral fractions as well as the bulk rock of Paris exhibit a positive $^{54}\text{Cr}$ anomaly. In contrast, the sequential dissolution pattern is similar to that of Murchison.

The $^{54}\text{Cr}$ values of both meteorites fall on the correlation line that has been established between $^{54}\text{Cr}$ and $\Delta^{17}\text{O}$ for carbonaceous chondrites [5]. In conclusion, the $^{53}\text{Cr}$ and $^{54}\text{Cr}$ isotope systems represent an efficient tool to decipher the origin and classification of meteorites.

---

**Intra-cratic lithospheric deformations — Heterogeneities, faulting and Rayleigh-Taylor instabilities**

WERONIKA GORCZYK1, BRUCE HOBB1, GUIZHI ZHU2, KLAUS GESSNER2 AND ALISON ORD2

1School of Earth and Environment, The University of Western Australia, Perth, Australia.
2Dept. of Geosciences, ETH-Zurich, Switzerland.

The seismological structure of the Earth’s lithosphere is identified to be strongly heterogeneous in terms of thermal and rheological properties. Lithospheric discontinuities are thought to be long lived and are mostly correlated with major tectonic boundaries that commonly have been reactivated and are subsequently the foci of magma intrusion and major mineralization. The occurrence of such variations may be caused for instance by amalgamation of micro-continents such as is thought to be characteristic of the Yilgarn, Western Australia or parts of South Africa.

This paper explores the control that 3D lithospheric heterogeneity exerts on the thermal and chemical evolution during deformation subsequent to the development of the heterogeneity, as well as periodicity and lateral distribution of phenomena such as Rayleigh-Taylor instabilities and fluid transport from the mantle through the crust. Exploration of the parameters controlling the 3D distribution of focusing mechanisms is crucial for understanding the distribution of major ore deposits along main structures. Empirical observations in Kalgoorlie area (Western Australia, Yilgarn craton) show that spacing of major gold deposits is approximately 30km along major lithospheric heterogeneities. This spatial distribution may result from periodic development of Rayleigh-Taylor instabilities along the contact zone, which results in fluid transfer in areas where delamination has occurred. From numerical experiments it appears that the yield strength of the weak zone is one important parameter controlling the spatial distribution of deformation.

Above the site of localised delamination of the mantle lithosphere, a series of deep crustal faults develop that may extend into the upper mantle. These deep structures can act as the pathways for mantle derived CO$_2$ ± H$_2$O fluids and alkaline igneous complexes.

---

Geochemical features of the fluvial plain sediments from the riverbank profiles of the metallogenic area of Eastern Serbia—Ecological significance

V. GORDANIC1*, M. VIDOVIC1, D. JOVANOVIC2 AND A. CIRIC2

1The University of Belgrade, IHTM, Dep. Ecol., Serbia (corresp:gordanicv@gmail.com; mivibgd@yahoo.com )
2Geological Institute of Serbia, Belgrade, Serbia (dramar@sezampro.rs; abciric@eunet.rs )

During the geochemical mapping of the Eastern Serbia region (in scale 1:1,000,000) samples from the river bank profiles of the drainage areas of several rivers were gathered. Samples (181) were taken from the A-horizons, overbank sediments and stream sediments of the different localities (56). Geochemical features of the area are preserved in the investigated river bank profiles. Significant Cu and Au deposits and smaller deposits of U, Fe and W exist in the area. The anomaly concentrations of the same metals are noted in the investigated river bank sediments.

Well preserved geochemical inscription in the river bank profiles is in good correlation with metallogenic features of this part of the Carpatho-Balkan geochemical province. Sampling network is adjusted to the hydrographical features and mapping scale. The most interesting results are presented in the table 1.

<table>
<thead>
<tr>
<th>locality</th>
<th>level</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Au</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mali</td>
<td>A</td>
<td>160</td>
<td>357</td>
<td>1610</td>
<td>0.20</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>OB</td>
<td>311</td>
<td>1065</td>
<td>3500</td>
<td>0.22</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>148</td>
<td>984</td>
<td>5444</td>
<td>0.25</td>
<td>8</td>
</tr>
<tr>
<td>Timok</td>
<td>A</td>
<td>20</td>
<td>3.0</td>
<td>60</td>
<td>140</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>OB</td>
<td>65</td>
<td>2.1</td>
<td>40</td>
<td>30</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>20</td>
<td>5.1</td>
<td>20</td>
<td>60</td>
<td>-</td>
</tr>
</tbody>
</table>

A= A-horizon; OB=overbank sediment; S =stream sediment

The results of gamma spectrometric analyses for 238U, 232Th and 40K reflect radiation burden of selected localities.

Geochemical inscription from the river bank profiles are significant for geochemical prospecting and for mineral raw material exploration, as well as for definition of anomalous concentrations areas of toxic and other elements.

This work has been financed by the Ministry of Science and Technology of the Rep. of Serbia, project OI 176018.

**Redox conditions in infiltration basins of a large scale soil aquifer treatment (SAT) of effluent**

O. Goren\(^1\), I. Gavriel\(^1\), A. Burg\(^1\), I. Negev\(^2\), J. Guttmann\(^3\), T. Kraitzer\(^2\), H. Chikurel\(^2\), W. Kloppmann\(^3\), C. Guerrot\(^3\) and M. Pettinat\(^3\)

\(^1\)Geological Survey of Israel, Jerusalem, Israel
\(^2\)Mekorot National Water Company, Tel Aviv, Israel
\(^3\)BRGM, Water Department, Orléans, France

Soil Aquifer Treatment (SAT) is considered to be an efficient and reliable effluent tertiary treatment system, in which the vadose zone and the aquifer serve as mechanical, geochemical and biological filters. In the SAT system of the Shafdan reclamation plant, Israel, large volumes of secondary effluent (about 130 million m\(^3\) annually) are recharged into the Costal Plain Aquifer and are recovered for irrigation after residence time of a few months in the aquifer.

A severe degradation of the reclaimed water quality occurs due to a sharp increase of the Mn concentrations. This enrichment is the result of sedimentary Mn-oxides reduction under suboxic conditions within the aquifer. Such conditions prevail in the aquifer due to the intensive organic matter oxidation and nitrification that take place in the upper part of the vadose zone and consume the dissolved oxygen from the recharged effluent [1].

The present work focuses on the redox reactions that occur in the infiltration basins as well as in the upper few meters below the basins, and aims to determine their sensitivity to different conditions, such as sunlight, temperature and recharge regime.

The preliminary results point to diurnal changes in the intensity of different redox reactions in the basins which have a significant impact on the redox conditions of the infiltrating effluents. The dissolved oxygen (DO) increases during the day to over-saturation values and decreases during night to under-saturation due to net photosynthesis and respiration, respectively. Unlike the DO, the dissolved organic carbon (DOC) in the effluents is quite stable during the 24-hour period. Moreover, the DOC concentrations in the water in the upper one meter of the vadose zone are higher than those in the basin. This implies that significant part of DOC oxidation takes place downward in the vadose zone. A combination of nitrogen mass balance and isotopic composition of oxygen and nitrogen in nitrates point to nitrogen removal by both NH\(_3\) volatilization and denitrification.


---

**An electrochemical approach to determine the redox properties of iron-bearing clay minerals**

Christopher A. Gorski\(^1\), Michael Sander\(^2\), Michael Aeschbacher\(^2\), Laura E. Klüpfel\(^1\) and Thomas B. Hofstetter\(^1,2\)

\(^1\)Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland
\(^2\)Institute of Biogeochemistry and Pollutant Dynamics (IBP), Swiss Federal Institute of Technology, ETH Zurich, Switzerland

Clay minerals often contain redox-active structural iron (Fe) that can participate in electron transfer reactions with several environmental constituents, including bacteria, biological nutrients, and pollutants. Despite significant work, the electron accepting/donating capacities and Fe\(^{2+}/Fe^{3+}\) reduction potential(s) remain difficult to access due to the lack of reactivity between clay minerals and electrodes.

In the current study, we have overcome this challenge by using organic electron transfer mediator compounds that rapidly react with both the clay mineral and the working electrode. Our approach uses chronocoulometry, where a fixed potential is applied (\(E\)) to the working electrode in a solution containing the mediator. The current (\(I\)) is then monitored after the addition of a known amount of clay mineral to quantify the number of electrons transferred. Electrochemical studies were complemented by batch experiments, where a solution of mediator at a set potential (\(E\)) is spiked with an aliquot of smectite and the change in potential is measured over time.

For these experiments, we have used an Fe-rich model clay mineral (ferruginous smectite, SWa-1). Highly reducing (\(E = -0.64\) V, SHE) and highly oxidizing (\(E = +0.61\) V, SHE) potentials led to the complete reduction and oxidation of the structural Fe of the smectite, respectively. At intermediate potentials, the Fe\(^{2+}/Fe^{3+}\) ratio has been measured as a function of \(E\), pH, and the reduction/re-oxidation cycles of the smectite. We find that the redox properties of structural Fe cannot be described by a single standard reduction potential (\(E^\circ\)); instead, the properties can be explained by either capacitor-like behavior or a distribution of local structures of octahedrally bound Fe with distinct \(E^\circ\) values. Additionally, the reduction/re-oxidation cycles of the smectite appears to strongly influence the Fe(II)/Fe(III) versus \(E\) relationship and the electron accepting/donating capabilities during Fe reduction and oxidation. The outcome of our study will help to address the biogeochemical implications of Fe redox reaction involving clay minerals.
Forensic analysis of surface fallout from low yield surface nuclear tests

RICHARD C. GOSTIC*, KIM B. KNIGHT, GREG SPRIGGS AND IAN HUTCHEON

Lawrence Livermore National Laboratory, Livermore, CA 94551, USA (*correspondance: gostic2@llnl.gov)

Five decades after the last US atmospheric test, fallout samples from low yield surface and near surface events are being re-examined for their forensic value using a combination of radiometric (counting) and mass spectrometry based techniques. Preliminary data from these studies indicate that soil samples collected along historical fallout plumes contain easily accessible information about key components of each test such as fuel isotopics and the elemental composition of structural components.

The distribution of fuel, activation product and fission product signatures as a function of soil grain size and distance from ground zero has been found to be nearly uniform among larger grain sizes of fallout soil (> 0.1 mm). Anthropogenic glasses extracted from the fallout soil samples constitute <5% of the bulk soil mass, yet contain >50% of the total activity. Order of magnitude increases in the concentrations of actinides such as $^{235}$U or $^{239}$Pu are observed in the glass relative to the soil. By gamma spectroscopy $^{235}$U concentrations are estimated to be >60 µg/g and $^{239}$Pu concentrations >20 µg/g in glasses recovered from two different tests. Preliminary analysis of the U bearing glasses by ICP-MS indicates a fuel with a minimum enrichment of 84% $^{235}$U. Further analysis of the stable isotope signal from ICP-MS measurements shows that Be is present in the glass at concentrations 4 times higher than in the soil, and that Cr, Co and Mo are present in the U bearing glasses at 3-20 times the bulk soil concentration.

These results demonstrate that fallout from low yield surface nuclear tests collected as surface deposits long after the detonation contains valuable information about device characteristics. This information is relevant to characterizing historical activities from surface based nuclear test programs and is applicable to nuclear forensics research. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-480552

Rapid esterifications for compound-specific stable isotope analysis of fatty acids

A.S. GOTO AND T. KORENAGA

Department of Applied Chemistry, Tokyo Metropolitan University, Tokyo 192-0397, Japan (*correspondance: akigoto@tmu.ac.jp)

Fatty acids are frequently found as abundant lipid molecules in biological and geological samples, and therefore have been employed as biomarkers in a number of studies particularly for organic geochemistry. However, to reduce polarity and enhance volatility of fatty acids, and resulting in improved shape and resolution of fatty acid peaks on gas chromatograms, derivatization such as esterification or silylation are generally required for identification and quantification as well as compound-specific stable isotope analysis (CSIA) of fatty acids.

Here we evaluate methyl (MCF) and ethyl chloroformate (ECF) derivatizations as a rapid and simple esterification for CSIA of fatty acids. These derivatizations are generally prepared with an admixture of MCF/H$_2$O/methanol/pyridine or ECF/H$_2$O/ethanol/pyridine at room temperature for 5 min (Fig. 1). In this study, we used 0.1M HCl aq., H$_2$O, 0.1M NaOH aq., or organic alcohol (methanol or ethanol) instead of H$_2$O to evaluate the efficiency of derivatization.

For both MCF and ECF derivatizations, fatty acids are esterified very rapidly (within 5 min) even at room temperature, and accuracy of the carbon isotope measurements is always less than 0.3‰ (1σ). Although the yield of derivatives would depend on the chemical constituents and pH of derivative reagents as well as on the carbon-chain length of fatty acids, quantitative esterification is observed by using ECF/ethanol/pyridine (2/60/5, v/v). Thus we conclude that these derivatizations are potentially suitable as a rapid and simple esterification tool for CSIA of fatty acids.

Figure 1: MCF or ECF derivatization of fatty acids.
U-Pb zircon geochronological, geochemical and Sr-Nd-Hf isotopic studies of granitoids in Muzhaerte River, Southwest Tianshan UHP belt (NW China), and their tectonic implications

L.L. GOU AND L.F. ZHANG*
The Key Laboratory of Orogenic Belt and Crustal Evolution, MOE; School of Earth and Space Sciences, Peking University, Beijing 100871, China
(*correspondence: Lfzhang@pku.edu.cn)

Two granitic intrusions, Changawuzi and Alasan plutons, in Muzhaerte River of Southwest Tianshan UHP belt (NW China) were studied, with the purposes of determining their ages, petrogenesis and implications for the evolution of South Tianshan orogenic belt. A SHRIMP zircon 206Pb/238U age of 333±3 Ma was obtained for the Changawuzi pluton and LA-ICP-MS zircon U-Pb dating gave three 206Pb/238U ages of 296±4 Ma, 292±2 Ma and 287±8 Ma for the Alasan pluton respectively. The Changawuzi pluton is formed in a continental marginal setting by fractional crystallization from the partial melting of juvenile mafic continental marginal arc rocks, which later assimilated ancient continental crustal material to the extent of 10-15% during emplacement as suggested by the Sr- Nd isotope mixing modelling. The elemental and Sr-Nd-Hf isotopic geochemical studies indicate that the Alasan pluton was the products of fractional crystallization of magma, which were generated by partial melting of mixture of crustal juvenile medium-to-high K intermediate-to-basaltic rocks and 10-30% ancient continental crustal material. As the closure of paleo-South Tianshan ocean (319 Ma), the lithospheric tearing with localized upwelling of asthenosphere occurred at the beginning of slab breakoff because of the localized deformation. This induced the syn-collision magmatism (317-301 Ma) in the Middle Tianshan terrane. Afterwards, the extensive upwelling of hot asthenosphere induced the partial melting of the crust and formation of voluminous granitic rocks in the early Permian (300-270 Ma) in the South Tianshan orogenic belt. These results imply successive stages of late subduction and closure of paleo-South Tianshan ocean, as well as the collision and post-collision between Tarim plate and Yili-Central Tianshan block happened in Late Paleozoic period.

Geochemical composition of recent sediments and subrecent variability of the last 500 years for the SW Adriatic Sea and the Gulf of Taranto (Southern Italy)

M-L.S. GOUEAU *AND G.J. DE LANGE
Department of Earth Sciences–Geochemistry, Faculty of Geosciences, Utrecht University, Utrecht, Netherlands
P.O. Box 80.021 3508 TA Utrecht
(*correspondence: m-l.goudeau@geo.uu.nl)

Previous studies from the Gallipoli shelf, Gulf of Taranto, S. Italy, indicate that continuous sedimentation at high accumulation rates and low bioturbation [1] permit high-resolution paleoclimate studies. Measurements of carbonate contents, thermoluminescence, oxygen and carbon isotopes, [2,3] and reconstructed sea surface temperatures [4] display cyclic frequencies similar to those known for solar cycles. Origin and processes related to these patterns, however, remain unclear. To study these cycles in more detail, a multi-proxy approach is needed to reconstruct e.g. changes in run-off, and productivity in the past. The Gulf of Taranto however is located in a coastal area, influenced by rivers, ocean currents, and eolian dust sources, affecting the geochemical composition of the in situ sediments [5-8]. Assessing input and geochemical fingerprints of all different sources to the Gulf of Taranto in the present system, will permit changes in these sources to be reconstructed. Here, we present details and interpretation for a compositional study of core top samples from the S. Adriatic and the Gulf of Taranto and terrestrial samples from the Italian Adriatic coastal area. Results are then used to reconstruct e.g. run off in the Gulf of Taranto for the last 500 years.

**Isotopic variations in mafic volcanic rocks from the western branch of the East African Rift**

D. GRAHAM*,†, T. FURMAN‡, J. BLICHERT-TOFT§, J. LUPTON¶, C. EBINGER¶ AND N. ROGERS¶

†College of Oceanic & Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA
‡Department of Gesciences, Pennsylvania State University, University Park, PA 16802, USA
§Laboratoire de Géologie de Lyon, Ecole Normale Superieure de Lyon, 69007 Lyon, France
¶NOAA/PMEL, Hatfield Marine Science Center, Newport, OR 97365, USA
¶Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY 14627, USA
¶Department of Earth Sciences, Open University, Milton Keynes, MK7 6AA, UK

Isotopic variations in lavas from regions of low tectonic extension, such as the western branch of the East African Rift (EAR), can be used to probe regional variability in the underlying continental lithospheric mantle. Volcanic rocks from the western branch of the EAR are isotopically among the most extreme young samples on Earth. Pb, Hf, Nd and Sr isotope compositions for mafic, undersaturated alkaline lavas from Rungwe, Kivu, Virunga and Toro-Ankole all show large variations over short lateral distances, indicating extensive isotopic heterogeneity in the continental lithospheric mantle source for these lavas, mostly due to ancient metasomatism from Rungwe, Kivu, Virunga and Toro-Ankole. Volcanic rocks underlying continental lithospheric mantle. Isotopic variations in mafic volcanic rocks from the western branch of the EAR are isotopically distinct compositions. In contrast, 3He/4He within each province shows a restricted range; 7.5-9.0, 5.0-6.5, 6.7-7.5 and 5.6-6.8 RA for Rungwe, Kivu, Virunga and Toro-Ankole, respectively. There is no evidence for the presence of high 3He/4He plume material such as that from a common mantle source beneath the western branch of the EAR, such as the lithosphere/asthenosphere boundary. In contrast, the distinct isotopic variations within each volcanic region represent the shallower, provincial characteristics of the underlying lithosphere.

**Electron shuttle production by Shewanella oneidensis**

JEFFREY A. GRALNICK* AND NICHOLAS J. KOTLOSKI

Department of Microbiology and BioTechnology Institute, University of Minnesota, St. Paul, MN, USA,
(*correspondence: gralnick@umn.edu)

**Extracellular Respiration**

Many dissimilatory metal reducing bacteria have evolved mechanisms to transfer electrons from the cytoplasmic membrane quinone pool to insoluble substrates (e.g. oxide minerals and electrodes) located beyond their outer membranes [1, 2]. Shewanella oneidensis strain MR-1 is the best understood model system for extracellular respiration. While biochemical evidence supports a direct mechanism for electron transfer to insoluble substrates, there is also strong physiological evidence for electron shuttling [3, 4]. Flavins (riboflavin and flavin mononucleotide (FMN)) were identified as the primary electron shuttle compounds produced by Shewanella. Our work seeks to define the contribution of electron shuttles to the reduction of insoluble substrates by S. oneidensis and understand the molecular mechanism underlying the production and processing of flavin shuttles produced by these bacteria.

**Discussion of Results**

We designed a mutagenesis screen in S. oneidensis to isolate strains that no longer accumulated flavins in culture supernatants. This work led to the identification of UshA, a 5’-nucleotidase involved in the processing of periplasmic flavin adenine dinucleotide (FAD) to FMN and adenosine monophosphate [5]. Strains defective in ushA accumulated FAD in culture supernatants instead of FMN or riboflavin. We repeated our mutagenesis screen in an ushA deletion mutant background to identify additional components involved in electron shuttle processing and secretion. This secondary screen identified mutants defective in flavin export and in electron shuttle production and secretion. Here, we present the characterization of the two new components related to electron shuttle regulation of flavin secretion. Here, we present the characterization of the two new components related to electron shuttle export by S. oneidensis. We have generated the first strain of S. oneidensis that is fully defective in electron shuttle secretion, allowing us to conclude that electron shuttling accounts for ~75% of the electron transfer activity to insoluble substrates. Moreover, electron shuttling mutants have no defect in respiration of soluble electron acceptors or chelated iron.

Deciphering mafic and felsic lunar magmatic events: Insight from zircon  

M.L. GRANGE1*, A.A. NEMCHIN1, N. TIMMS1,  
R.T. PIDGEON1 AND C. MEYER2  
1Dept. of Applied Geology, Curtin University, GPO Box 1987,  
Perth, Western Australia 6845. (*correspondence:  
m.grange@curtin.edu.au)  
2NASA Johnson Space Center, Houston, TX 77058, USA.  

Microstructural studies of zircon grains from lunar breccia samples, combining high resolution imaging together with in-situ U-Th-Pb analyses, has allowed us to distinguish primary zircon, formed by igneous crystallisation in plutonic rocks, and secondary, impact-related, features in zircon grains. Dating of these grains can be used to identify multiple igneous and impact events. For example, a single impact melt breccia from the Apollo 17 landing site contains grains that record more than 3 igneous events in addition to 3 distinct impact events, indicating that the region sampled by this breccia probably significantly exceeds the area of the landing site. As a result, the study of primary zircon ages in the available samples can be used to investigate the temporal distribution of plutonic magmatism on the Moon, even though these samples were collected from the relatively small areas covered by the lunar landing missions.

The study of primary zircons containing inclusions of rock-forming minerals or zircons preserved in lithic clasts found in lunar breccias also provides an opportunity to place temporal constraints on the different types of plutonic magmatism on the Moon. U and Th concentrations of these zircon grains vary systematically allowing clear separation of zircons formed in mafic rocks, such as anorthosite, norite, and gabbronorite, from those formed in felsic rocks (i.e. granophyre and felsite). This chemical variation can be used to determine plutonic hosts of zircon grains found as mineral clasts in the breccia samples and as loose grains in lunar soils, expanding significantly the number of zircons with known origin.

A comparison of ages of zircons originating from mafic and felsic host rocks suggests a possible age difference between these two chemical rock groups. If confirmed by further analyses this would indicate that the two current explanations for the formation of felsic rocks on the Moon, (i) as residual melt left after extreme fractionation of basaltic magma or (ii) as a result of liquid immiscibility during late stages of fractionation of basaltic melts, are incorrect. Both mechanisms imply close temporal relationships between mafic and felsic rocks, which does not appear to be supported by the available U-Pb ages.

Silicon isotopes as a tracer for silicate utilization in the Peruvian upwelling  

PATRICIA GRASSE*, CLAUDIA EHLERT,  
LOTTHAR STRAMMA, EVGENIYA RYABENKO,  
JASMIN FRANZ AND MARTIN FRANK  
IFM-GEOMAR, Wischhofstr. 1-3, 24148 Kiel, Germany  
(*correspondance: pgrasse@ifm-geomar.de)  

Natural stable isotopes are a powerful tool in marine sciences to investigate biological processes, such as present and past nutrient utilization. In this study we present the first dissolved silicon isotope data in the upwelling area off Peru, where one of the world’s largest Oxygen Minimum Zones (OMZ) is located. Samples were recovered during “FS Meteor” cruises M77/3 and M77/4 in 2009. Silicic acid is the most important component required for the growth of diatoms, which dominate the primary productivity in this region. Stable silicon (Si) isotopes are fractionated during diatom growth in that the lighter isotopes are preferentially incorporated into diatom frustules with a fractionation factor of -1.1‰. The Si isotope composition of dissolved silicic acid of the corresponding surface waters is therefore left isotopically heavier. The silicon isotope composition, δ30Si/28Si is given relative to a reference standard (NBS28) and expressed in the δ30Si notation. Dissolved Si isotope signatures of seawater provide a measure for the degree of utilization of silicic acid but are also influenced by water mass mixing. Surface waters on the shelf off Peru are mainly fed by the Peru Chile Undercurrent (δ30Si=1.5‰), which consists of water masses ultimately originating from the western and Central Pacific. In areas and during phases of intense upwelling the fractionation of Si isotopes was observed to be weaker due to upwelling driven supply of less fractionated Si (δ30Si=1.8‰) from water depths of 50 to 150m, whereas under weak upwelling conditions the surface waters are heavier (δ30Si=2.8‰) due to more complete utilization of the available dissolved silicic acid. The distribution of the dissolved silicon isotope compositions correlates strongly with particulate biogenic silicate (opal) concentrations in that the highest opal concentrations in surface waters on the shelf reflect the lowest δ30Si values thus the strongest upwelling intensity. The most extreme δ30Si values in surface waters (δ30Si=3.2‰) are observed offshore where silicic acid is limited. Furthermore we compare δ30Si data with the dissolved nitrogen isotope distribution, which, in addition to nitrate utilization, is also influenced by denitrification and annamox processes in the OMZ. Combined silicon and nitrogen isotope compositions can thus help to disentangle different fractionation processes within the nitrogen cycle.
Chemical modification of airborne mineral dust

VICKI H. GRASSIAN
Department of Chemistry, University of Iowa, Iowa City, IA 52246, USA (vicki-grassian@uiowa.edu)

Introduction
Mineral dust aerosol, i.e. suspended soil particles, can impact a wide range of global processes including the chemistry of the Earth’s atmosphere and the Earth’s climate. Atmospheric processing of mineral dust through heterogeneous chemical and photochemical reactions will modify the properties of the dust particle and thus alter how these particles impact global processes [1-3].

Approach
Using a combined approach of applying state-of-the-art surface sensitive probes, aerosol instrumentation and reactivity studies provides for an understanding of reactions on dust particles and how these reactions can alter the global impacts of mineral dust aerosol. These laboratory studies can provide a conceptual framework from which to understand the details of chemical processes that modify the properties of mineral dust aerosol as these particles are transported through the atmosphere [4].

Discussion of Results
The importance of mineralogy, the link between interfacial chemistry and climate and the specificity of mineral dust aerosol chemistry will be discussed. Examples will be shown that clearly provide evidence to show that mineral dust modifies the chemical balance of the atmosphere through heterogeneous reactions and that heterogeneous reactions modifies the physicochemical properties of mineral dust particles.


Stable isotopes of organics and inorganics of Aptian lacustrine sediments in North-Eastern Brazil

R. GRATZER1*, V.H. NEUMANN2, W. VORTISCH1, D. ROCHA2 AND A. BECHTEL1
1Montanuniversität Leoben, 8700 Leoben, Austria, (*correspondence: gratzer@unileoben.ac.at)
2Universidade Federal de Pernambuco, Recife, Brazil (neumann@ufpe.br, dunaldson@msn.com)

The Jatobá Basin is located in the Pernambuco-Alagoas massif, NE Brazil. The elliptical basin, orientated NE-SW, is characterized by a semi-graben structure with tilted blocks toward NW direction. The analysed section [1] consists of shales, marls, sandstones, limestones and dolostones.

Stable isotope analysis was carried out on carbonates and organic matter. TOC content varies from 0.5-13 wt%, Hydrogen and Oxygen Indecies from 6 to 715 and 4 to 44 respectively. The organic matter is immature (R0 % 0.28) and is represented by kerogen Type I in the lower section. In the upper section it is modified by the addition of terrestrial organic matter. A ~3 m thick clay-rich shale seperates the the sections.

<table>
<thead>
<tr>
<th></th>
<th>Lower section</th>
<th>Upper section</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ13C Carbonates</td>
<td>-8.72 to -3.65</td>
<td>-3.57 to +2.47</td>
</tr>
<tr>
<td>δ18O Carbonates</td>
<td>-8.09 to -4.98</td>
<td>-8.67 to -4.11</td>
</tr>
<tr>
<td>δ13C Pr + Ph</td>
<td>-28.25 to -31.66</td>
<td>-31.66 to -30.28</td>
</tr>
<tr>
<td>δ13C C29 Steranes</td>
<td>-26.59 to -30.12</td>
<td>-30.12 to -28.08</td>
</tr>
<tr>
<td>δ13C C30 Hopanes</td>
<td>-27.40 to -32.96</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Table 1: Variation and trends in δ13CpDB ‰ and δ18OpDB ‰ of carbonates and δ13CpDB ‰ organic compounds.

δ18O of carbonate minerals (Table 1) indicates fresh water conditions throughout the sediment column. In the deepest part of the lower section dolomite occurs together with high TOC contents. Here δ13C suggests intense microbial activity during carbonate formation. In contrast, δ13C shift to more positive values in the upper part, indicating less microbial influence. The upward trend of organic δ13C is towards lighter values in the lower section and heavier values in the upper section (see Table 1). This is interpreted as the result of changing environmental conditions and enhanced terrigeneous organic matter input.

Hydrogeochemical survey of CO₂ geological leakage using noble gases: Application to the Furnas Caldera (Azores, Portugal)

C. GREAU1,2*, M. MOREIRA1, P. AGRINIER1, V. LAGNEAU2, H. SCHNEIDER3, P. MADUREIRA4 AND L. RUZIE1

1Institut de Pysique du Globe de Paris (IPGP), 1 rue Jussieu, 75005 Paris, France (*correspondence : greau@ipgp.fr)
2École des Mines de Paris, Centre de Géosciences, 35, rue Saint Honoré, Fontainebleau, 77305 Cedex, France
3EDF R&D, Site des Renardières, Route de Sens, Écuelles, Moret-sur-Loing, 77818 Cedex, France
4Universidade de Évora, Centro de Geofísica de Évora, Departamento de Geociências, 8 Rua Romão Ramalho, 59, 7000-671 Évora, Portugal

Significant natural CO₂ emissions have been measured across the caldera of Furnas (São Miguel Island, Azores) allowing us to consider the area as a CO₂ leakage analogue. During two field trips, we have collected twenty springs in purpose to measure CO₂ contents (Dissolved Inorganic Carbon and δ¹³C) and noble gas isotopic compositions (He and Ne) and for seventeen water samples, major ions chemistry. The corrected 3He/4He ratios (normalized to air ratio Rₐ) range from 1.46 to 5.17, the carbon contents (DIC) range from 0.57 to 41,41 mmol/l and most of the waters have a δ¹³C about -4 ‰.

With field observations and waters chemistry, we have characterized seven different types of water springs through the caldera, resulting from various mixing rates between three sources : soil equilibrated meteoritic water, gas emanations (CO₂, He...) from a magmatic intrusion and hydrothermal waters coming from a shallow depth aquifer. Saturation indexes and geothermometers indicate a trachytic aquifer at a temperature of about 145°C.

In order to confirm that noble gases are good tracers of CO₂ leakage, we are building a first mixing model using noble gases and carbon isotopes and a second one based on major ions chemistry with CHESS hydrochemical modelling software. Preliminary mixing models seem to be consistent thus confirming that noble gases can be used as tracers of CO₂ leakage.

Comparison of Diviner Lunar Radiometer Observations of Apollo sites and Apollo soils measured in simulated Lunar environment


1JPL, Caltech, Pasadena, CA 91109, USA (*correspondence: Benjamin.T.Greenhagen@jpl.nasa.gov)
2Univ. of Oxford, Oxford, OX1 3PU, UK
3NASA Johnson Space Center, Houston, TX 77058, USA
4Brown Univ., Providence, RI 02912, USA
5Univ. of California, Los Angeles, CA 90095, USA

The Diviner Lunar Radiometer (Diviner), onboard NASA’s Lunar Reconnaissance Orbiter, has made the first direct global measurements of lunar silicate mineralogy using multispectral thermal emission mapping [1]. Diviner has three spectral channels near 8 μm designed to characterize the Christiansen feature (mid-infrared emissivity maximum) [2], which systematically shifts to shorter wavelengths with increasing silicate polymerization [e.g. 3,4].

Only laboratory experiments conducted in simulated lunar environment (SLE) are directly comparable to Diviner data. The Lunar Thermal Environment Simulator at University of Oxford’s Atmospheric, Oceanic, and Planetary Physics Laboratory is uniquely capable of measuring thermal emission of samples in SLE [5]. In the lunar environment, large thermal gradients develop in the top few hundred microns of the surface, driven by the difference in the solar and thermal skin depths (i.e. the surface is heated to greater depth than the infrared emitting layer). The thermal gradients generally result in a significant enhancement of Christiansen feature spectral contrast and significant decreases in Reststrahlen Bands spectral contrast.

Diviner observations include all six Apollo sites at approximately 200 m spatial resolution. Spectral differences between the Apollo sites caused by composition and space weathering are apparent in Diviner data [1]. Since the compositions of Apollo soils are known, the Apollo sites are important calibration points for the Diviner dataset. This presentation will include the first comparison of Diviner observations of Apollo sites and spectra of Apollo soils measured in SLE.

Surface modifications of engineered nanoparticles and their impacts on cytotoxicity

KELVIN B. GREGORY1,2, ZHIQIANG LI1,2 AND GREGORY V. LOWRY 1,2
1Carnegie Mellon University, Civil and Environmental Engineering, Pittsburgh, PA, 15213, USA
2Center for Environmental Implications of Nanotechnology

The interactions of engineered nanoparticles (ENP) with the natural environment will have a deterministic affect on their fate and transport, yet the impacts of environmental transformations of ENP are poorly understood. For example, previous work in our laboratory demonstrated that bare particles of nanosized zero-valent iron exhibited toxicity towards bacterial cells at concentrations as low as a few mg/L, yet oxidation of the iron surfaces or the presence of natural or engineered coatings may eliminate the toxic effects of NZVI. We examined the impact of surface transformations on the bacterial toxicity of ENP through the application of natural and/or engineered coatings on the particles. We selected particles with different mechanisms of expressing cytotoxicity; 1) NZVI- requires direct contact with cells, 2) TiO2- produces reactive oxygen species, and 3) AgNP- produce toxic metal cations. Our findings show that both natural and engineered surface coatings on NP may greatly reduce or eliminate the cytotoxicity of NP. However, the ability and mechanism of interference with toxicity is dependent on both the type of particle as well as the coating. While engineered coatings of NZVI induced electrostatic or electrosteric repulsion between the NP and cell that prevented toxicity, the natural organic matter coatings scavenged reactive oxygen species. Interestingly, engineered polyaspartate coatings did not prevent the toxicity of TiO2. The coating of AgNP with engineered and natural polymers has little impact on toxicity, but oxidation of the surface through sulfidation greatly reduced toxicity. Our studies imply that surface modifications may be engineered to minimize cytotoxicity and that the potential for detrimental impacts of ENP in the environment is lessened by coatings on which arise in natural systems.

Physical versus chemical non-equilibrium model for simulating U(VI) adsorption

JANEK GRESKOWIAK1,2,*, MICHAEL B. HAY3, HENNING PROMMER2, CHONGXUAN LIU4, VINCENT E. A. POST5, RUI MA6, CHUNMIAO ZHENG6, JAMES A. DAVIS3 AND JOHN M. ZACHARA4
1University of Oldenburg, 26111 Oldenburg, Germany
(*correspondence: janek.greskowiak@uni-oldenburg.de)
2CSIRO Land and Water, Wembley, Australia
3USGS, Menlo Park, USA
4Pacific Northwest National Laboratory, Richland, USA
5Flinders University, Adelaide, Australia
6University of Alabama, Alabama, USA

Surface complexation reactions and diffusional mass-transfer between mobile pore water and immobile water associated with the intra-grain pores have been found to play an important role for the overall U(VI) transport behaviour in the US DOE Hanford 300A aquifer. Several laboratory- and field-scale scenario simulations have been carried out to investigate the behaviour of two alternative model approaches for the simulation of coupled intra-grain diffusion and surface complexation of U(VI) under dynamic groundwater flow and hydrochemical conditions.

The physical non-equilibrium approach explicitly calculates aqueous speciation and surface complexation in the intra-grain pore spaces as instantaneous reactions and simulates the diffusional mass-exchange between the mobile and immobile domains by a set of multiple 1st-order rates. The chemical non-equilibrium approach approximates the diffusion-limited surface complexation by a multiple 1st-order kinetic reactions, which makes it computationally efficient compared to the physical non-equilibrium approach. While for linear sorption scenarios the two model approaches are equivalent, they show differences when the sorption process becomes non-linear, for example as a result of surface complexation reactions under varying hydrochemical conditions.

Under the Hanford 300A field scale hydrological and hydrochemical conditions, the two model approaches predicted largely similar U plume behaviour. In contrast, simulated U(VI) mass discharge into the Columbia River that is adjacent to the 300A was noticeably higher in the physical model due to a higher degree of non-equilibrium in the plume fringe located at the river-groundwater interface. However, compared to other effects, such as that of calcite dissolution on U(VI) mass discharge, the choice of the non-equilibrium model approach appeared to be less important.
Experimental determined standard properties for MgSO₄·4H₂O (starkeyite) and MgSO₄·3H₂O; A revised internally consistent thermodynamic dataset for magnesium sulfate hydrates

K.-D. GREVEL¹,², J. MAJZLAN¹, A. BENISEK¹, E. DACHS¹, M. STEIGER³, A. D. FORTES⁵ and B. MARLER²

¹Inst. of Geosciences, Friedrich-Schiller University, Jena, Germany (*correspondence: Klaus-Dieter.Grevel@rub.de)
²Inst. for Geology, Mineralogy and Geophysics, Ruhr-University, Bochum, Germany
³Dept. of Materialscience & Physics, Mineralogy Division, University Salzburg, Austria
⁴Dept. of Chemistry, University of Hamburg, Germany
⁵Dept. of Earth Science, University College London, UK

A number of different hydrated forms of MgSO₄·nH₂O (1 ≤ n ≤ 11) are known to exist on Earth and also on Mars. Recently, the enthalpies of formation from the elements (ΔfH²⁹⁸) of kieserite (n = 1), sanderite (n = 2), hexahydrate (n = 6), and epsomite (n = 7) were measured [1]. Now, we have obtained ΔfH²⁹⁸ of synthetic MgSO₄·3H₂O and MgSO₄·4H₂O (starkeyite) by solution calorimetry in water at T = 298.15 K. The resulting values are –2210.3 ± 1.3 and –2498.7 ± 1.1 kJ mol⁻¹ for the trihydrate and starkeyite, respectively.

The standard entropy of starkeyite was derived from low-temperature heat capacity measurements using a PPMS® Diamond DSC in the temperature range 280 K < T < 295 K. The resulting values are –2210.3 ± 1.3 and –2498.7 ± 1.1 kJ mol⁻¹ for the trihydrate and starkeyite, respectively.

Additionally, DSC measurements with a Perkin Elmer Diamond DSC in the temperature range 280 K < T < 295 K were performed to check the reproducibility of the PPMS® measurements around ambient temperature. All Mg sulfate hydrates change their hydration state in response to the local temperature and humidity conditions.

Based on recently reported equilibrium relative humidities [3] and the new standard properties described above, the internally consistent thermodynamic database for the MgSO₄·nH₂O system [1] was refined.

The geogenic impact on groundwater composition in the Netherlands

JASPER GRIFFIOEN12*, SOPHIE VERMOOTEN2 AND BAS VAN DER GRIFT 2
1TNO Geological Survey of the Netherlands, Utrecht, the Netherlands (*correspondence: jasper.griffioen@tno.nl)
2Deltares, Utrecht, the Netherlands

The quality of groundwater is vital for both its natural function and anthropogenic use. Surprisingly, the geogenic control on groundwater composition has received little attention while the petrological composition of the rock matrix forms a major factor on groundwater composition. We have systematically investigated the geogenic control on both major groundwater composition and a series of trace elements at a national scale for the Netherlands. Several thousands of existing groundwater analyses were classified on geological formation. Additionally, the samples were grouped into 26 unique geographical regions. Regional statistics were created for all solutes of interest. An interpretation was established in terms of salinity, pH and carbonate status, redox status and nutrients. Interesting regional differences are noted within both the Pleistocene part of the Netherlands where phreatic aquifers are dominant, and the Holocene part where a reactive layer of clay and peat lies at the surface. This holds both for the major groundwater composition as well as for trace elements. These differences can partly be related to the sedimentary origin of the deposits, where marine deposits are more reactive than fluvial deposits. Upon result, the buffering capacity of marine deposits is larger but the natural contamination with arsenic, nutrients and salinity, too. This buffering capacity is monitored by an additional field and laboratory campaign, which establishes regional statistics on reaction capacities of sediment.

The crystal chemistry of (As,Sb,Bi)-bearing dumortierite

L.A. GROAT1*, R. JAMES EVANS1, E.S. GREW2 AND A. PIECZKA3
1University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada (*correspondence: lgroat@eos.ubc.ca)
2University of Maine, Orono, Maine 04469-5790, U.S.A
3University of Science and Technology, 30-059 Kraków, Poland

Dumortierite [c. (Al,Fe)Al6(BO3)Si3O13(O,OH)2] and holtite [c. (Ta,Fe)Al6(BO3)(Si,As,Fe)3O12(O,OH,Fe)3], are isostructural minerals found in a few granitic pegmatites. Dumortierite may contain several wt.% of SbO3, As2O3, Ta2O5, thereby blurring compositional distinctions between the two, although generally As > Sb in dumortierite. For this study we investigated the effect of minor amounts of Sb and As on the crystal structures of dumortierite samples D21 (Rats quarry, Hartmannsdorf, Saxony), D31 (Tonagh Island, Enderby Land, Antarctica) and D27 (Uval'dy Lake, Il'men Mountains, southern Urals, Chelyavinskaya Oblast', Russia). Average electron microprobe compositions for sample D21 show 2.32 wt.% As2O3 (0.14 atoms per formula unit) and 0.57 wt.% Sb2O3 (0.02 Sb apfu); for D31, 2.85 wt.% As2O3 (0.18 apfu) and 1.03 wt.% Sb2O3 (0.04 apfu); and for D27, 1.69 wt.% As2O3 (0.10 apfu) and 0.68 wt.% Sb2O3 (0.03 apfu). Analyses of samples D21 and D27 show no appreciable Ta, whereas sample D31 contains on average 1.62 wt.% Ta2O5 (0.04 apfu). Sample D27 also contains Bi (1.07 wt.% Bi2O3, 0.03 apfu).

Crystal structure refinements of single-crystal X-ray diffraction data converged to R1 values 1.92, 1.62, and 3.04% for samples D21, D31, and D27 respectively (all D27 crystals investigated were twinned in the normal fashion for dumortierite, with three twin individuals related by 120° rotation about a threefold twin axis parallel to a). For all three samples the results suggest that the As and Sb atoms are at the Sb1 and Sb2 sites, as is the case for holtite. However in the dumortierite samples the atomic displacement parameters (ADPs) associated with the atoms at these sites are unusually large, with \( U_{ab} \) Sb1 values of 0.03 Å\(^2\), 0.02 Å\(^2\), and 0.09 Å\(^2\), and \( U_{ab} \) Sb2 values of 0.02 Å\(^2\), 0.03 Å\(^2\), and 0.06 Å\(^2\), for samples D21, D31, and D27, respectively (for holtite these values are generally less than or equal to 0.01 Å\(^2\)). Atomic displacement parameters for the coordinating oxygen atoms are no larger than in holtite and dumortierite with no As or Sb.

The reason for the large ADPs remains under investigation but may be a function of the small amounts of As and Sb at these sites, or perhaps indicates the presence of both trivalent and pentavalent As and Sb (and perhaps Bi, or Bi\(^{3+}\) and Bi\(^{5+}\)) at the Sb1 and Sb2 positions.

Mineralogical Magazine  www.minersoc.org
Reconstruction of permanent thermocline temperatures in the Atlantic during Heinrich Stadial 1
J. GROENEVELD1*, C. M. CHIESSI1, A. MACKENSEN2 AND R. TIEDEMANN3
1Marum Excellence Cluster, Alfred Wegener Institute, Bremerhaven, Germany
(*correspondence: Jeroen.Groeneveld@awi.de)
2School of Arts, Sciences, and Humanities, University of São Paulo, São Paulo, Brazil
3Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

Changes in Atlantic Meridional Overturning Circulation (AMOC) have been modeled to lead to a global adjustment of the depth of the thermocline via the propagation of Kelvin waves, particularly in the North Atlantic with warming during AMOC slowdown. The aim of this study is to test for significant warming during AMOC shutdown by reconstructing permanent thermocline temperatures for the Deglaciation at key locations in the Atlantic. Therefore, we used Mg/Ca-paleothermometry on the deep-dwelling foraminifer *Globorotalia inflata*.

We established a new Mg/Ca-temperature calibration for *G. inflata* based on core top samples from the South Atlantic. The reconstructed apparent calcification depth for dominantly non-encrusted specimens is 350-400 m making *G. inflata* ideal to reconstruct temperature changes in the permanent thermocline.

First results from core GeoB9508-5 off northwest Africa, which is close to the boundary between the predicted thermocline warming (to the north) and cooling (to the south), show a significant warming during HS1 of ~4°C supporting the prediction of subsurface warming in the North Atlantic during AMOC slowdown. Interestingly, this warming occurs after the actual start of HS1.

Temporal dynamics of arsenic-bearing phases during the suspended transport
C. GROSBOIS1*, A. COURTIN-NOMADE2, E. ROBIN3, H. BRIL2, N. TAMURA4, J. SCHAERF5 AND G. BLANC5
1Université François Rabelais de Tours. UMR 6113 CNRS ISTO. Tours, France
(*correspondence: cecile.grosbois@univ-tours.fr)
2Université de Limoges. EA GRESE IFR 145 GEIST. Limoges, France
3Université d’Orsay. LSCE, UMR CEA/CNRS 1572. Gif sur-Yvette, France
4ALS, LBNL, Berkeley, California USA
5Université de Bordeaux 1. UMR 5805 CNRS EPOC. Talence, France

In a former gold mining district (Isle river basin, France), arsenic-bearing phases have been characterized in suspended particulate matter by in-situ techniques (EPMA, SEM-EDS/ACC system and synchrotron based μXRD) in order to describe the temporal dynamics of As at a particle scale during the solid transport.

The most frequent As-bearing phases but the least As-concentrated (0.10-1.58 wt% As) were aggregates of various fine clay particles (chlorite-phlogopite-kaolinite assemblage during the high flow and chlorite-illite- muscovite assemblage during the low flow). They were also associated to Fe-coatings and nano- to micro- particles of Fe oxyhydroxides like goethite (0.18 - 0.45 wt% As, Fig. 1).

Iron and Mn oxyhydroxides were the 2 other types of As-bearing phases (0.12-2.80 wt% As and 0.14-1.26 wt% As respectively), present as discrete particles. Their occurrence and in-situ concentrations varied throughout the hydrological cycle, according to their detrital or newly formed origins.

![Figure 1](image)

**Figure 1**: BSE image of a grain of Fe oxyhydroxyde associated to μ-XRD maps representing the relative abundance of a- goethite (4.18 Å), b- chlorite (7.07 Å) and c- muscovite (9.9 Å).
Birefringence mapping: A new in situ mass-loss technique for determining mineral solubilities

Juliane Gross1,*, Michael Burchard1 and Walter V. Maresch1

1Lunar and Planetary Institute, Houston TX 77058, USA
2University of Wroclaw, W. Cybulskiego 30, 50205 Wroclaw, Poland

Data for the solubility of minerals in aqueous solutions at high pressures and temperatures are essential for our understanding of fluid properties, mass transport and growth/dissolution processes of minerals in Earth’s crust and upper mantle. [e.g. 1-4].

Although a fairly extensive dataset is now available on the solubility of minerals in aqueous fluids at high pressures, most of the data above 0.5 GPa have been obtained by ex situ weight-loss quench methods in piston-cylinder presses [e.g. 5-7]. However, the uncertainties are generally large and difficult to quantify, because the resulting phase assemblages and product textures are characterized at post-experimental conditions. This can be problematic for the interpretation of the results if phase transitions, quench crystallization, incongruent dissolution or mechanical fragmentation occurred.

We developed a new in situ mass-loss technique for hydrothermal diamond anvil cell experiments that uses the fact that crystals show birefringence in polarized light. Birefringence depends on the crystal’s phase difference and its thickness. By measuring the phase difference at every point on a crystal, the thickness of the crystal at every such point can be determined and its surface area mapped. By multiplying the thickness of the crystal with its surface area its volume can be calculated. The mass of a crystal is then given by its volume multiplied by its density. With this method crystal masses less then a few μg can be determined.

This new method combines the advantages of ex situ and in situ approaches, such as direct observation of the reaction path of the sample while circumventing their obvious disadvantages, such as quench problems.


Antimony and arsenic behaviour upon microbial dissolution of mining waste

M. Grybos1,*, J. Kierczak2, O. Rakotoarisoa1, A. Courtin-Nomade1 and H. Bril1

1University of Limoges, GRESE Laboratory, FST, 123, avenue A. Thomas, 87060 Limoges Cedex, France
2University of Wroclaw, W. Cybulskiego 30, 50205 Wroclaw, Poland

In surface and sub-surface environment, microorganisms mediate dissolution and precipitation processes of minerals, and thus affect geochemical cycling of elements. Antimony (Sb) and arsenic (As) are considered to have comparable geochemical behavior and toxicity, both are redox sensible and toxic even at low concentrations. In natural environment, weathering of mining waste is one of the major source of contamination by metal(loid)s including Sb and As. Determination of biotic factors influencing Sb and As mobility is crucial to understand geochemical behaviour of these elements in environment.

In this study, we performed controlled incubations of mine tailings containing > 0.2% and 0.06% of Sb and As respectively under abiotic and biotic (phylogenetically divergent heterotrophic bacteria) conditions to assess the role of bacteria on As and Sb release upon dissolution process. Role of microbes (biotic factor) was evaluated by comparing the amount of a given element released during biotic incubation to the amount of the same element released during abiotic incubation at the same pH value.

The results shown that all used bacteria were able to weather highly contaminated solids. For a given pH value, the amount of released Sb and As varied between the strains and was from half-fold less to three-fold greater than under abiotic conditions. This indicates that complexing metabolites produced by bacteria play an important role in the overall dissolution process and may have accelerating or inhibiting effect on Sb and As release. Positives correlation coefficients of biotic factors between Sb and Fe (R² = 1), Ca (R² = 0.58), and Al (R² = 0.999) as well as negative correlation coefficients of biotic factors between As and Fe (R² = 0.58), Ca (R² = 0.98), and Al (R² = 0.57) suggest its different behaviour upon microbial dissolution.

In conclusion, heterotrophic bacteria influence Sb and As geochemical pathway and mobility in environment.

Mineralogical Magazine www.minersoc.org
Features of the pyrites in black shale series in Southern Anhui Province

YOUFEI GUAN1,2, YONG ZHAN1,2, HAIJIAO YOU1,2, GUODONG SHI2 AND MAOYAN MA2

1China Gezhouba Group Corporation, P.R. China
(631677428@qq.com)
2Anhui University of Architecture, P.R. China

Black shale series in southern Anhui Province are located widely and belong to Lower Yangtze depression area, mainly developing the Sinian and Early-Middle Triassic sedimentary cover, late Yanshanian intrusions, and Indosinian-Early Yanshanian NE Jura-type folds and a series of the NE thrusting (sliding) nappe structure.

According to the crystal habit of the pyrite crystals in black shale series in southern Anhui Province, the pyrites can be divided into five crystal forms: {100} cube, {100}+{200} cube and pyritohedron combination, {111} octahedron, {210} pyritohedron and {210}+{111} pyritohedron and octahedron combination. The Co/Zn ratios of pyrites with various crystal forms are relatively low, mostly less than 0.15. The As content of the pyrite with {100} + {200} crystal form is the highest (120 ppm), and that of the pyrite with {111} crystal form is about 32 ppm on average that is many times higher than claystone’s (6.6 ppm).

The Co/Zn ratios of sediments can distinguish their different sources. The Co/Zn ratio for hydrothermal origin is relative low, with value of 0.15 on average, and that in iron-manganese crust or concretion is about 2.5 in general. Therefore, the Co/Zn ratios can be used as a sensitive indicator to distinguish the source of sediments. The Co/Zn ratios of the pyrites from black shale series in southern Anhui Province indicates that the pyrites have features of strong hydrothermal deposit.

Many studies suggest that hydrothermalism is the key for the formation of noble metal deposits in black shale series. This conclusion has been proved in Hunan-Guizhou. The pyrite’s features and genesis indicate that the noble metals may enrich and even form deposit in black shale series in southern Anhui Province.

This research was financially supported by the Natural Science Foundation of Anhui Province Provincial Education Department of China (NO.KJ2010A070).

Mineral paragenesis and textural features of gneisses and amphibolites from Daday-Devrekani (Kastamonu, Turkey) Massif: Preliminary results

M.A. GUCER1* AND M. ARSLAN2

1Dept. of Geol. Eng., Gümüşhane Univ., 29100-Gümüşhane, Turkey (*correspondence: maligucer@gmail.com)
2Dept. of Geol. Eng., Karadeniz Tech. Univ., 61080-Trabzon, Turkey (marslan@ktu.edu.tr)

The Daday-Devrekani (Kastamonu, N Turkey) massif contains various metamorphic rocks ranging from Precambrian to Early Cretaceous in age [1]. NE part of the massif contains medium to high grade metamorphic rocks, called Devrekani Metamorphics [2], and divided into two sub-units; gneissic rocks of the lower parts and calcite marbles of the upper parts. In this study, gneissic and amphibolitic rocks of the massif were examined in terms of mineral assemblages and textural evidence of metamorphic P-T conditions. The gneissic rocks are biotite-hornblende, cordierite-biotite, sillimanite-biotite, sillimanite-cordierite-mica, sillimanite-garnet-mica, sillimanite-cordierite-garnet-mica, microcline-biotite, muscovite-microcline-biotite and sillimanite-garnet-cordierite-microcline-biotite gneisses. They contain quartz, K-feldspar (orthoclase, microcline), plagioclase, biotite, muscovite, sillimanite, cordierite, garnet, hornblende, sericite, Fe-Ti oxide, zapatite, zhemaitie, zircon, hercynite (?). The amphibolitic rocks contain hornblende, oligoclase-andesine, Fe-Ti oxide and zoisitoclase. The rocks exhibit grano-, lepidograno-, fibrolepidograno-, nemato-, nematograno-, lepidonemato- and porphyro-lastic textures. In some gneiss, there are pre-kinematic and syn-kinematic mineral growth, and cordierite porphyroblasts containing sillimanite, hercynite (?) and garnet inclusions.

Possible mineral reactions in gneissic rocks are as (1) Muscovite + quartz → K-feld. + sillimanite + H2O, (2) chloride + muscovite (or chloritoid) + quartz → garnet + biotite + H2O, (3) garnet + sillimanite + quartz → cordierite, (4) sillimanite + garnet → cordierite + hercynite, (5) biotite + sillimanite + plagioclase + quartz→garnet + cordierite + K-feld. + H2O. Possible mineral reaction in amphibolites is albite + actinolite + epidote + chlorite → plagioclase (An>17) + hornblende. All these features suggest amphibolite facies P-T conditions.

Dissolution rates of plagioclase feldspars as a function of solution composition

S. GUDBRANDSSON1*, D. WOLFF-BOENISCH2, S.R. GISLASON2 AND E. H. OELKERS1

1GET-Université de Toulouse-CNRS-IRD-OMP, 14 Avenue Edouard Belin, 31400 Toulouse, France
2Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavik, Iceland

Feldspars are the most abundant mineral in the Earth’s crust and plagioclase is the most abundant of these feldspars. Plagioclase dissolution is therefore a major, and at times dominant, contributor to global weathering rates. It is therefore remarkable how little work has been performed to systematically characterize the dissolution rates of this mineral as a function its composition and the composition of the fluid phase.

Towards the improved characterization of the dissolution behaviour of the plagioclases in natural processes, the steady-state dissolution rates of 5 distinct plagioclase feldspars, spanning the compositional range from albite to anorthite, have been measured in mixed-flow reactors at 25 °C as a function of pH from pH 2 to 11. Rates tend to exhibit a typical U-shape behaviour; rates decrease with increasing pH at acidic conditions, then increase with increasing pH at basic conditions. Similar to past work [1, 2] plagioclase dissolution rates increase with increasing An content at acidic conditions. In contrast, preliminary work suggests little effect of An content at basic pH.

Interpretation of the dissolution rates of the plagioclase feldspars is challenging because this mineral tends to consist of finely intergrown albite rich and anorthite rich phases. To address this challenge, measured rates have been interpreted assuming the dissolving plagioclase is a mechanical mixture of two distinct end-member feldspars similar to that done recently for the dissolution of crystalline basalt [3].


3H – 3He isotopic tracer for age estimating of the ground waters (Aquifers of the Khibiny slopes, Kola Peninsula)

ANTON GUDKOV1*, IGOR TOLSTIKHIN1 AND STANISLAV IVANOV2

1Russian Academy of Science, Kola Science Center, Geological Institute
2Russian Academy of Science, Kola Science Center, Institute of the North Industrial Ecology Problems

To introduce the 3H - 3He method samplers of stainless steel and degassing of water, using the flow of water vapor through the capillary as a gas – carrier have been developed and made. When being pumped through the capillary almost all helium and neon (over 95%) is collected in the trap. At the same time gets not more than 0.5 grams of water (i.e. approximately 0.3% of the sample mass, Beyerle et al., 2000) gets in the trap. The extraction and purification processes take approximately 30 minutes. The water samples were taken from the bores located at the southern slope of the Khibiny mountains (the Kola peninsula). The picture shows the measured relations of $^{3}$He / $^{20}$Ne and $^{3}$He in the samples from water inlets “Centralniy” (the grey squares, the figures are numbers of the bores Kamensky et al., 1991) and “Klyuchevoy” (the grey circles). In these coordinates the mixture of young waters (the corresponding points, the square and the circle are located above the coordinates of the air saturated water, ASW) and the deep ancient waters (in the lower left corner of the graph, the radiogenic He is formed in enclosing rocks, and migrating from them, is accumulated in ground waters) is expressed in the straight line. Regression line extrapolation of the samples from the water inlet “Centralniy” (the black line on the graph) to the trend ASW + $^{3}$He gives $^{3}$He / $^{4}$He = 3, 65 × 10^{-6}. Concentration of the $^{3}$HeTRI gives $^{3}$H - 3He isotopic tracer for age estimating of the ground waters (Aquifers of the Khibiny slopes, Kola Peninsula)
The use of magnetic susceptibility in forensic soils analyses

A. GUEDES*, H. RIBEIRO, H. SANT’OVAIA, A. RODRIGUES, B. VALENTIM, S. LEAL AND F. NORONHA

Centro de Geologia da Universidade do Porto e Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, Porto, Portugal, (*correspondence: aguedes@fc.up.pt)

Magnetic parameters such as magnetic susceptibility (MS) are important in characterizing materials, and detectable quantities of magnetic and paramagnetic minerals are almost always found in soils, the magnetic susceptibility being the sum of all contributions from the forming minerals, and varying due to concentration and composition of those minerals. The MS measurements of soils at room temperature are non-destructive. Therefore, the same material is available for further analysis with any other technique. Additionally, does not require sample preparation, and can be used as a simple and fast method which may be operable in small samples. So, MS is an excellent tool for studies of soils being used as trace evidence in forensic investigations.

Magnetic susceptibility measurement methodology, discriminatory power, reproducibility and accuracy in analysis were tested on soil samples for its use in forensic applications. Seventeen soil samples were collected on several Portuguese sites surrounded by different lithologies. At each site, samples were manually collected from the surface soil with a plastic spade. The magnetic susceptibility was measured applying an external magnetic field of 300 A/m to the sample, and a Kappabridge, model KLY-4S of Agico balance equipped with the Sumean software was used. Tests were performed on each sample to establish the discriminatory power between similar and different geological and geographical origins; the measurement reproducibility within samples and along the time; the variation with sample quantity, size fractions and presentation method. Before each measurement, the equipment was calibrated, and regularly calibrated along the measurement period due to the repeated nature of the measurements carried out. Magnetic susceptibility was calculated in m³/kg. It was observed that magnetic susceptibility can enable discrimination between soil samples, measured values are reproducible over time, and the analysis can be carried out in samples as small as 0.5 g.

This research was supported by Project PTDC/CTE-GEX/67442/2006 of FCT (Portugal).

Chemical and isotopic properties of airborne particles in industrial, urban and rural areas of the Rhine Valley

F. GUÉGUEN1,2, P. STILLE1, V. DIETZE3 AND M. MILLET2

1Laboratoire d’Hydrologie et de Géochimie de Strasbourg, Université de Strasbourg/EOST, CNRS; 1 rue Blessig, F-67000 Strasbourg
2Equipe de Physico-Chimie de l’Atmosphère, Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, Université de Strasbourg/ECPM, CNRS; 1 rue Blessig, F-67000 Strasbourg
3German Meteorological Service, Research Center Human Biometeorology; Stefan-Meier-Str.4. D-79104 Freiburg

In order to evaluate the past and actual air pollution, tree barks (biomonitoring) and airborne particulate matter (dp >2.5 µm) were collected around and within the industrial area of the cities of Strasbourg (France) and Kehl (Germany) situated on both sides of the river Rhine. Theses cities suffer from emissions of traffic and industries (steel plant, thermal power plant and waste incinerators) located in the industrial harbour.

Sr, Nd and Pb isotopic ratios measured on barks allowed to distinguish between various sources of pollution. Traffic emissions are the main contaminants in the urban areas of the cities, whereas local industrial emission plumes are distinguishable around and within the industrial harbour.

Organic and inorganic emissions were monitored during 9 months by Sigma-2 passive samplers as well as by passive air samplers with XAD-2 resin for PCB collection for actual air quality measurement in these environments. Sample sites were located in remote, rural and in urban areas, where different industrial emission plumes have been detected by tree bark biomonitoring.

Ambient aerosol collected in these different environments have similar trace element concentrations but the mass deposition rate is highest in the industrial zone. Enrichment factors (EF) ((X/Nd)/(X/Nd) UCC) are particularly high in Mn, Cr, Zn, Mo, Cd, and similar to EF measured in tree barks. Isotopic ratios of the collected particles from different sampling sites allowed to distinguish between anthropogenic and natural sources. The dominating emission source in the industrial area is the steel plant as also demonstrated by the aerosols trace metal concentrations. Both organic and trace metal emissions are correlated, which allows the Sr and Nd isotopes to be a powerful tool to trace the polluting sources.
Isotope fractionation during Fe translocation in plants grown with an artificial chelate

M. GUELKE-STELLING1* and F. VON BLANCKENBURG2
1KIT, Inst. for Mineralogy and Geochemistry, D-76131 Karlsruhe (*correspondence: monika.stelling@kit.edu)
2GFZ Potsdam, D-14473 Potsdam (fvb@gfz-potsdam.de)

The determination of the plant-induced Fe-isotopic fractionation with multiple-collector ICP-MS is a promising tool to better quantify their role in the geochemical Fe cycle and possibly to identify the physiological mechanisms of Fe uptake and translocation in plants.

We show here that half of the entire range of Fe isotope variations detected to date on this planet (-2.5‰ in δ56Fe) occurs when Fe is moved within a single plant. This finding extends that of an earlier study in which we found that strategy I plants, which rely on reduction of iron before uptake, were enriched in stable 54Fe relative to 56Fe when grown on soil. In contrast strategy II plants (grasses), which rely on chelation of Fe(III) by phytosiderophores before uptake, were slightly enriched in the heavier iron isotopes [1,2].

In our new study bean plants (strategy I) and oat plants (strategy II) were grown in a nutrient solution supplemented with Fe(III)-EDTA, and were harvested at three different ages. All parts of the plants during all growth stages were quantified for Fe amounts and isotope composition. Total bean plants, regardless of their age, were found to be enriched in the light iron isotopes by -1.2‰ relative to the growth solution throughout. However, during growth plants internally redistributed isotopes where young leaves increasingly accumulated the lighter isotopes whereas older leaves and the total roots were simultaneously depleted in light iron isotopes. For bean fruits, mass balance indicates that these obtain ca. 40% of their Fe from translocation within the plant (with δ56Fe = -2.65‰) and 60% from the roots. Given that not all of this fruit Fe can be supplied by older leaves, the roots apoplastic plays a major role as intermediate Fe store. Both apoplastic Fe and tissue-bound Fe is remobilised by reduction – preferring the light Fe isotopes. In contrast, during growth of the oat plants the initial isotope ratio obtained during uptake is maintained in all organs at all growth stages, including the roots. Hence it can be assumed that both uptake and translocation of Fe in strategy II plants maintains the iron’s ferric state, or that Fe is always bound to high-mass ligands, so that isotope fractionation is virtually absent in these plants.


The nitrogen isotopic composition of a Proteozoic microbial community

NUR GUENELI* and JOCHEN J. BROCKS
Research School of Earth Sciences, The Australian National University, Canberra, A.C.T. 0200, Australia (*correspondence: nur.gueneli@anu.edu.au)

Nitrogen is an essential element for life, incorporated into fundamental components such as amino acids and DNA. The isotopes of nitrogen can be used to trace biogeochemical processes, yet, the use of this tool to reconstruct Precambrian environments is still in its infancy. Recent studies on nitrogen isotope fractionation in microorganisms [1,2] have significantly improved interpretations of paleorecords [3-5] and the use of nitrogen isotopes in combination with established biomarker techniques has now the potential to yield novel information about the succession of predominant primary producers through deep time.

The 1.64 Ga Barney Creek Formation (BCF), northern Australia, represents a marine succession deposited below wave base in the intracratonic McArthur Basin. The dolomitic shales of the BCF bear the oldest preserved, clearly indigenous molecular fossils [6]. Based on these biomarkers, the upper BCF marks a marine basin with anoxic, sulphidic, sulphate-poor and stratified waters inhabited by green and purple phototrophic sulphur bacteria (PSB) [7]. Evidence for these PSB disappears in deeper successions. However, it is currently under debate whether the lack of PSB derives from biological or thermal degradation, or a shift in ecological settings. Here, we will present 15N and 13C data in combination with biomarker analysis to test whether regime changes caused a shift in predominant primary producers in the McArthur Basin.


Mineralogical Magazine www.minersoc.org
Fluid inclusion analysis by laser ablation ICPMS: How consistent are element ratios?

MARCEL GUILLONG1*, THOMAS PETTKE2 AND LEONID DANYUSHEVSKY1

1CODES, ARC Centre of Excellence in Ore Deposits, University of Tasmania, Private Bag 79, Hobart, TAS, 7001, Australia
(*correspondence: marcel.guillong@utas.edu.au)
2Institute of Geological Sciences, University of Bern, Baltzerstrasse 1 + 3, CH-3012 Bern, Switzerland

Analysis of fluid inclusions is a commonly used technique to obtain insights into fluid evolution and ore forming processes. Laser ablation ICPMS offers the possibility to analyse individual inclusions for a wide range of elements and certain isotope ratios, with low detection limits. Quantification of inclusion composition is commonly performed by normalising measured element signals to those of Na or Cl, which are used as internal standards, with their concentrations determined via micro thermometry.

Using a Resonetics M-50 laser probe which allows for analysis of fluid inclusion at depths up to several hundred microns, we observed that values of some element signal ratios change between shallow inclusions and deep inclusions by up to a factor of 2.5. This limits the accuracy of inclusion analysis at larger depth from the sample surface. The Cl/Na and the Pb/Na ratios were found to be affected the most. Ablating a scapolite sample with homogeneous Na, Pb and Cl concentrations showed very similar behaviour. Such strong fractionation behaviour of chlorine has not been reported to date for LA-ICPMS analysis. This may account for some of the scatter observed when analysing a series of individual fluid inclusions, as inclusions are commonly located at a range of depth below the surface. Results from two different brine assemblages will be presented and discussed.

Figure 1: Aspect ratio dependent Cl/Na ratios for scapolite mineral and a fluid inclusion assemblage.

U-Pb SHRIMP and geochemical data of granitoids characterizing the evolution of shear zones in NE Brazil

I. P. GUIMARÃES1*, A.F. SILVA FILHO1; F.M.V. SILVA2 AND R. ARMSTRONG3

1Depto de Geologia –UFPE
(*correspondence: ignez@ufpe.br)
2Geologia - UFPE, Petrobrás (francismiller@hotmail.com)
3RSES - Australian National University (richard.armstrong@edu.edu.au)

A large volume of granitic magmatism associated with large scale shear zone and metamorphism under high-T conditions, characterize the Brasiliano/Pan African Orogeny in the Borborema Province, NE Brazil. Granitoids from two plutons and later dykes intruded along a large dextral sense E-W trending Shear Zone show distinct crystallization ages and geochemical signature. The oldest studied granitoids (U-Pb SHRIMP age of 618 ± 5 Ma), Serra de Inácio Pereira Pluton (SIPP), show high Ba (4440 to 6654 ppm) and Sr (2358 to 2962 ppm) and medium to high Zr (321 to 378 ppm), low Y (19 a 25 ppm) and Nb (14.7 to 17.0 ppm) contents. Their REE patterns are characterized by small or no negative Eu anomalies (Eu/Eu*= 0.92 – 1.15) and (Ce/Yb)$_n$ ratios ranging from 28.34 to 40.09. In contrast, the granitoids showing crystallization age of 563 ± 4 Ma, the Serra do Marinho Pluton (SMP) have low Sr (238 to 272 ppm), and high Zr (755 to 846 ppm) contents. The contents of Y (40 to 75 ppm) and Nb (9.0 to 51.0 ppm) are higher and the Ba (1660 to 1680 ppm) contents lower compared to the values recorded in the SIPP granitoids. Their REE patterns are characterized by negative Eu anomalies (Eu/Eu*= 0.39 – 0.59) and (Ce/Yb)$_n$ ratios ranging from 6.62 to 20.25. Later dykes of subvolcanic granitoids have crystallization ages of 527 ± 6 Ma and A-type geochemical signature. The SIPP granitoids are coeval with the peak of regional metamorphism and originated by melting of a paleoproterozoic source. The SMP show geochemical signature of post-collisional A-type granites and the later dykes have signature of A-type post-orogenic extension-related granitoids coeval with the deposition of small sedimentary basin.
Microbial diversity in Oylat Cave and their roles on biogeochemical cycling

YASEMIN GULECAL* AND MUSTAFA TEMEL

Istanbul University, Istanbul, Turkey
(*correspondence: ygulecal@istanbul.edu.tr)

The subsurface of the Earth is one of the major habitats and contains a significant proportion of microbial life [1, 2]. However, our overall knowledge about the life forms and biogeochemical processes contained within it is rather scarce, mainly because of the difficulties in approaching this habitat. One relatively easy way to approach this habitat is to investigate karst terrains, which expand over ~20% of the Earth's subsurface [3]. Since caves are one of the most prominent features of karst terrain, they may serve as noteworthy entries and virtual "windows" into subsurface habitats [4].

Recent work has revealed interesting insights into the diversity and resilience of different life forms in caves may be revealed and how to recognize biosignatures for subsurface life on other planetary bodies [for example,5-6].

Our studying area which is Oylat Cave in Bursa (Turkey) has been developed at the intersection of two fault zones striking along WNW-ESE and NE-SW directions in recrystalized limestone unit of Permian-Triassic age. Clastics and carbonate sediments are in the Oylat Cave developed due to karstification. The aim of study was to investigate the microbial diversity and their roles of biogeochemical cycling.

We have not only used the geochemical analyses but also genetic tools. In addition, this study reports the first microscopic investigations on the microbial communities encountered in the microbial biofilm Oylat Cave.


Geochronology of Cenozoic intrusive rocks of NW Anatolia: Topkaya-Eskişehir, Turkey

B. GULLU* AND Y.K. KADIOĞLU

Ankara Univ., Department of Geol., Eng., & YEBIM Ankara, Turkey (*correspondence: bgullu@ankara.edu.tr)

The intrusive rocks of Northwest Anatolia mainly exposed at Sivrihisar, Karakaya and Topkaya region of Eskişehir in Sakarya continent. Topkaya (Eskişehir) Granitoid is intruded into the metamorphic basement and obducted ophiolitic suite in the composition of granodiorite, monzogranite and cutting by felsic and mafic dykes. They have MME ranging from 1cm up to 60cm in sizes [1].

The 40Ar/39Ar age data reveal 44.30 ± 0.47 Ma for granodiorite of Topkaya granitoid. The isotopic ratio of granitoids and mafic dykes of the Topkaya have almost same (87Sr/86Sr)i and BNd ratio (87Sr/86Sr)granodiorite=0.705593-0.706133, BNd-granodiorite= -0.6, -0.7; ((87Sr/86Sr)mafic dyke =0.705677-0.705706, BNd mafic dyke= -0.39, -0.4).

Discussion and Results

The 40Ar/39Ar age and geochemistry may be interpreted to reflect the time of magmatism since the level of emplacement was shallow enough such that rapid cooling would have occurred.

The granitoid exhibited initial rates 87Sr/86Sr always less to 0.708, suggesting represent I-type granites [5]. Sm-Nd data show distinct isotopic signatures, to the granitoid and mafic dykes. Both units exhibited εNd initials values clear negative, suggesting crustal contribution with mantle products in the source.

The authors wish to thank Ankara University for support BAP 09B4343016 Project.

Hydrochemical properties of thermal waters in the Eastern Black Sea section

FATMA GULTEKIN*, ARZU FIRAT ERSOY AND ESRA HATIPOGLU

Karadeniz Technical University, Department of Geological Engineering, 61080, Trabzon, Turkey
(*correspondence: gultekinftma@hotmail.com)

The Iliça (Artvin), Ayder and İkizdere (Rize) and Sarmaşık (Ordu) thermal waters are located Eastern Black Sea section. Thermal springs and thermal wells have temperatures ranging from 37 to 70°C. The pH values of the thermal waters change between 6.32 and 8.92. Thermal waters display various chemical compositions and high temperature waters have Na-SO₄, Na-HCO₃ and Na-Cl type. In the Ordu and Artvin area Late Cretaceous and Eocene aged volcanic rocks constitute reservoir and cap rocks. Late Cretaceous aged granite, granodiorite and monzonite rocks are reservoirs and cap rocks in the Rize geothermal system. The water-rock interaction has been investigated in this study. The thermal waters located rocks dominate region in the Gibbs Diagram. The chemistry of thermal water is controlled by weathering of minerals containing the rocks. According to chemical analysis basaltic rocks have higher Co, Sr, V, Cu, Pb, Zn, Ni and As content than granitic rocks. Especially Iliça, İkizdere and Sarmaşık thermal waters have high As, B, Ba, Br, Fe, Li, Rh, Cs and Zn concentration. Compare with Rare Earth Elements (REE) content rocks and thermal waters La, Ce, Nd and Pr are immobile elements for Ayder and Sarmaşık thermal waters. Iliça and İkizdere thermal waters are similar to REE content.

Duofuton mafic volcanic suite at northeastern margin of the Qing-Tibet plateau: Its age, geochemistry and tectonic implications

A. GUO, X. HU, Y. GUO, C. ZHANG AND L. ZHANG

State Key Lab of Continental Dynamics/Department of Geology, Northwest University, Xian 710069, China
(anlingxb@nwu.edu.cn)

Located at the northeastern margin of the Qinghai-Tibet Plateau, the Duofuton volcanics belong to a Na-rich and mafic volcanic suite. The suite has yielded an age of 96.21±2.10 Ma by the whole-rock ⁴⁰Ar/³⁹Ar method, indicating a magmatic product in early Late Cretaceous time.

The rocks are characterized by the (La/Yb)₀ ratios of 6~11, ⁸⁷Sr/⁸⁶Sr of 117, enrichment in incompatible elements. The Nb/U and Ce/Pb ratios are 30 and 17 on average, respectively. The ⁸⁷Sr/⁸⁶Sr ratios of the samples are 0.7041~0.7069, ¹⁸⁷Os/¹⁸⁷Os =0.5129 (~ 6) and ⁴⁰⁶Pb/²⁰⁶Pb and ⁴⁰⁶Pb/²⁰⁷Pb =11 ~ 19 and 73~84. Coupled with high ⁸⁷Sr/⁸⁶Sr ratios, they show Dupal anomalies. The rocks are OIB-like in nature and their source region exhibits mixture between DM and EMII, while some samples are contaminated by continental crust. The complexity of the OIB-like rocks may have inherited from the proto- and paleo-Tethyan mantle in the region and is possibly not related to materials of eastward extrusion from the plateau. Compared with the contemporaneous volcanics in the area, it can be inferred that the mantle region below at the northeastern margin is heterogeneous. The development of the volcanic activity in the area could be triggered by the distance effect from the initial collision between the Eurasian Plate and a microcontinent in northwest Indian Plate.
Using Mössbauer spectra to characterize and differentiate tourmaline crystals from China

Y. GUO1, S.Y. YANG2*, J.H. MIN1, L.J. WANG1 AND Y.B. XIA1

1School of Materials Science and Engineering, Shanghai Uni., Shanghai 200072, China,
2State Key Lab. of Marine Geology, Tongji Uni., Shanghai 200092, China (*correspondence: syyang@tongji.edu.cn)

Tourmaline is a valuable crystalline raw material notable for its piezoelectric and pyroelectric properties. It is also regarded as precious stones in jewelry industry. Tourmaline occurs in almost all types of geologic circumstances and coexists with numerous minerals. Consequently, chemical variation of tourmaline is tightly related with its crystal structure and physical properties which provides important constraints on the origin of tourmaline. Mössbauer spectra analysis has been playing an important role in the detailed study of isomorphic substitutions in tourmaline crystal by Fe2+ and Fe3+ and the distribution of these ions over distinct crystallographic positions. Nevertheless, the traditional research on Mössbauer parameter of tourmaline crystals has great uncertainty in the determination of the valance states and occupation types by the experience values.

In this contribution, the multi-statistic method of cluster analysis was used to effectively determine the Mössbauer spectra and examine microscopic structures of Fe ions in different tourmaline crystals from Guangxi, Hebei, Neimeng and Xingjiang Provinces where have much variable geologic background. The determined assignment corresponds well with previous documented results. We observed four kinds of distribution styles of iron (Fe) ion in the measured tourmaline samples, which distinctly occupy four zones in the diagram of isomer shift and quadrupole splitting. The tourmaline crystals from Guangxi, Hebei and Neimeng are characterized by similar Mössbauer spectra bearing three doublets, which correspond to Fe2+(Y), Fe2+(Z) and Fe3+(Y) sites with two kind of valances respectively. In comparison, only two doublets appear in the Mössbauer spectrum of Xinjiang tourmaline, and the Fe ions having bivalence states occupy Fe2+(Y) and have a neighborhood effect in the Y-Z site. Our study on Mössbauer spectra together with scanning electronic microprobe analysis clearly suggests these tourmaline crystals sourced from different areas have variable compositions and crystalline structures indicative of their different origins.

This work is supported by Supported by NSFC (Grant No: 60676002, 41076018) and Shanghai Municipal Education Commission, Shanghai, China (Grant No:06AZ007)

Long term aerosol trends over large global urban centres

PAWAN GUPTA1,2*, MAUDDOD N. KHAN2 AND ARLINDO DA SILVA1

1NASA Goddard Space Flight Center, Greenbelt, MD, USA (*correspondence: pawan.gupta@nasa.gov)
2Universities Space Research Association, Huntsville, AL, USA (maudood.n.khan@nasa.gov, arlindo.dasilva@nasa.gov)

Aerosol Optical Depth (AOD) retrieved from MODIS and MISR sensors onboard EOS Terra satellite over the last decade (2001-2010) has been utilized to analyze aerosols trends over global megacities. Analysis provides an assessment of retrieval capabilities of these sensors. Level 2 data sets have been carefully analyzed over selected urban centers to understand the retrieval capabilities of these two sensors over complex urban surfaces. Areas over each urban center have been identified, where MODIS operational algorithm is unable to retrieve AOD due to limitation of dark target approach. MISR aerosol product has been used to identify dominating aerosol size distribution and type, as function of seasons. Spatial gradient in AOD within and around the city has been estimated as well. Impact of spatial and temporal averaging over long term trends will also be addressed.

Figure 1: Annual mean aerosol optical depth from MODIS (Terra) over Karachi, Pakistan for 2001 to 2010.
Conduit-scale to localized degassing in ascending magmas: Insights from Cl measurements in Vesuvius 79AD pumice

L. GURIOLI1, T. SHEA1*, E. HELLEBRAND1 AND J.E. HAMMER1

1 LMV, Univ. Blaise Pascal, Clermont-Fd, France
2 SOEST, Univ. Hawaii, 1680 East-west rd., Honolulu, HI, 96822, USA (*correspondence tshea@hawaii.edu)

During the ascent and decompression of magmas that fed the 79AD eruption, melts experienced a complex vesiculation history [1]. Both textural evidence from tephra and conduit ascent modelling suggest that velocity gradients affect the ascending magma column and cause spatial variations in degassing [2]. Localized shearing is one of the dominant mechanism through which these velocity gradients can be accommodated during ascent [3]. These shear zones can enhance bubble connectivity and provide pathways for volcanic gases. Here, we present chemical evidence for spatial degassing variations at the scale of the conduit as well as at localized scale. Because Cl diffuses slower than H2O during ascent, it records a different portion of the magma’s history. Figure 1 below shows Cl increases within denser more degassed zones in 79AD pumice clasts. Through textural observations of vesicles as well as Cl and H2O measurements within pumice glass from various phases of the 79AD eruption, we derive a general conduit model that involves the birth, development, and death of shear-zones.

Soil source contribution estimation of Arsenic and Lead in atmospheric precipitaion at urban industrial area, Raipur, Central India

BALAKRISHNA GURUGUBELLI AND SHAMSH PERVEZ
School of Studies in Chemistry, Pt. Ravishankar Shukla
University, Raipur, INDIA. 492010

The components and quantities of atmospheric dust fallout have been reported to be the pollution indicator of large urban areas. The multiplicity and complexity of sources of atmospheric dusts in urban regions has put forward the need of source apportionment of these sources indicating their contribution to specific environmental receptor. The study presented here is focused on investigation of soil source contribution estimates of Arsenic and lead in urban dust fallout in an urban-industrial area, Raipur, India. Source-receptor based representative sampling plan using longitudinal study design has been adopted. Source apportionment has been done using Chemical Mass Balance (CMB 8). Dominance of coal fired industries sources on arsenic levels measured at selected ambient residential receptors compared to line sources has been observed. Road-traffic has shown highest contribution of dust at indoor houses and out door-street automobile exhaust has shows highest contribution for arsenic. The results of CMB output and regression data of source-receptor dust matrices have shown comparable pattern.

Figure 1: Compositional map (Cl=blue, K=red, Si=green) made in 79AD pumice. Cl increases towards the denser zone richer in large collapsed vesicles (left) likely due to degassing of H2O. Image width ~ 0.5mm.

**Calcium isotopes in Martian meteorites**

N. GUSSONE1, T. MAGNA1 AND K. MEZGER2

1Universität Münster, Germany  
(Nikolaus.Gussone@uni-muenster.de, tomas.magna@uni-muenster.de)  
2Universität Bern, Switzerland  
(klaus.mezger@geo.unibe.ch)

Mass-dependent fractionation of Ca isotopes at high temperatures has long been considered minor; consequently, Ca isotopes have mostly been used to study low-temperature processes [1,2]. Here we report high-precision Ca isotope data for a suite of Martian meteorites revealing a δ44/40Ca variation of ~0.4‰ among shergottites, nakhlites, chassignites and orthopyroxenite. Calcium isotope ratios of Martian crust generally fall into the range of terrestrial basalts but tend to be slightly heavier than Earth's crust. δ44/40Ca exhibits no clear relationship with modal contents of olivine, plagioclase and/or pyroxene although pyroxene is the main Ca carrier in the mantle [3]. No systematic behavior is observed between individual groups of shergottites, despite the range in element depletion/enrichment, suggesting a lack of Ca isotope fractionation imparted by different degrees of melting. δ44/40Ca of 1.06 in orthopyroxenite ALH 84001 is in the mantle range whereas low δ44/40Ca in NWA 2737 may reflect the presence of carbonate minerals. Nakhlites mostly have distinctive δ44/40Ca similar to terrestrial plume basalts [4], supporting the derivation of nakhlites from a Martian mantle plume. Whether this difference is directly linked to the dominance of clinopyroxene (with generally lower δ44/40Ca) in nakhlite lavas or is an intrinsic feature of nakhlite mantle source remains to be solved. Nevertheless, Ca appears to evolve distinctively different isotope ratios in plumes and mantle rocks, providing evidence for resolved Ca isotope fractionation at magmatic temperatures.

Collectively, the new data suggest δ44/40Ca ~1.0–1.1 for the bulk silicate Mars. This is identical to an estimate of the Earth's upper mantle [3] and suggests broadly similar processes for mantle melting in the interiors of Mars and Earth, independent of time constraints on the activity of mantle dynamics. Unlike other stable isotope systems, the bulk Ca isotope composition of Earth and Mars differs from enstatite chondrites [5,6]. Thus, they are probably not the major building material for Earth and possibly not for Mars.


**Lead(II) sorption to soil materials – Binding heterogeneity and influence of phosphate**

J.P. GUSTAFSSON1, C. TIBERG2, A. EDKYMISH1 AND D.B. KLEJA1

1KTH (Royal Institute of Technology), Department of Land and Water Resources Engineering, Teknikringen 76, 100 44 Stockholm, Sweden. (gustafjp@kth.se)  
2Swedish University of Agricultural Sciences, Department of Soil and Environment, Box 7014, 750 07 Uppsala. (Charlotta.Tiberg@slu.se)  
3Swedish Geotechnical Institute, Kornhamnstorg 61, 111 71 Stockholm. (Dan.Berggren.Kleja@swedgeo.se)

Lead (Pb) is a common pollutant, but still the environmental behaviour of lead is incompletely known. Attempts to simulate the binding of lead(II) to soils by use of geochemical models have usually underestimated lead binding with about one order of magnitude.

Here, new evidence will be presented about some key mechanisms that can explain the failure of most previous modeling attempts. First, the adsorption of Pb2+ to ferrihydrite, an important Pb2+ sorbent in soils, is shown to be very strong, particularly at low Pb2+/ferrihydrite ratios. Second, the sorption of Pb2+ to ferrihydrite is greatly enhanced in the presence of phosphate. The effect is stronger than that predicted by electrostatic interactions only. The mechanisms involved are being studied with spectroscopic methods.

Third, data will be presented that show that the sorption of Pb2+ to solid-phase organic matter, especially moor layer material, is much stronger than that of fulvic or humic acid, which are often used as model compounds for solid-phase organic matter. Apparently, Pb2+ is strongly bound to a non-humic organic fraction of the solid-phase organic matter, but the mechanism by which this occurs remains obscure. Taken together, these observations may explain the often observed deviation between model and reality concerning lead(II) binding.
Lack of a late deglacial carbonate compensation signal in the intermediate depth Amundsen Sea

M. GUTJAHR1,2,*, D. VANCE1, J.W.B. RAE1, G.L. FOSTER2, C.D. HILLENBRAND3 AND G. KUHN4

1Bristol Isotope Group, Department of Earth Sciences, University of Bristol, Queens Road, Bristol BS8 1RJ, UK (*correspondence: marcus.gutjahr@noc.soton.ac.uk)
2School of Ocean and Earth Science, National Oceanography Centre, Southampton, UK
3British Antarctic Survey, High Cross, Madingly Road, Cambridge CB3 0ET, UK
4Alfred Wegener Institute for Polar and Marine Research, Am Alten Hafen 26, 27568 Bremerhaven, Germany

The Southern Ocean (SO) is an important component in deglacial ocean circulation- and climate change. Ice core-derived temperature and atmospheric pCO2 records show a deglacial rise as early as 17.9 ka [1, 2], thereby leading Northern Hemisphere warming by about three thousand years [3]. The atmospheric CO2 rise occurred alongside increasing bioproductivity around Antarctica, providing evidence that reinvigorated upwelling of Circumpolar Deep Water (CDW) around Antarctica led to large-scale degassing of Dissolved Inorganic Carbon (DIC) stored in the glacial deep ocean [4]. Changing CDW circulation patterns should also find their expression in variable CDW DIC/alkalinity relationships. In broad terms, the release of previously deep-sea stored DIC to the atmosphere should leave deglacial CDW more alkaline until the excess alkalinity is removed from the water column. To test this hypothesis we have measured the boron isotopic composition (expressed in δ11B) of calcitic scleraxonian cold-water corals sampled in intermediate water depths in the Amundsen Sea (~123°W, ~69°S, 2500 m to 1430 m water depth). We will present an assessment of the genus-specific biological fractionation (c.f. [5, 6]) alongside fossil-coral δ11B values dating back to the Antarctic Cold Reversal. Our corals appear to be internally homogenous and modern samples have only slightly elevated δ11B compared to that of ambient intermediate water borate ion. We find that modern and early Holocene coral display fairly constant δ11B compositions, whilst deglacial coral δ11B are slightly elevated. This suggest that the deglacial evolution of the deep Southern Ocean carbonate system is more complicated than a simple degassing and carbonate compensation model may indicate.


The emergence of metabolism: Prebiotic simulations of shallow sea hydrothermal vents

MARCELO I. GUZMAN

Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA (marcelo.guzman@uky.edu)

The origin of metabolism has been one of the most challenging and intriguing issues in the origin of life research. All known carbon fixation pathways used by living organisms, including the reductive tricarboxylic acid cycle, share at least one common intermediate [1]. The implications are that 1) all carbon fixation mechanisms are linked, and 2) a prebiotic mechanism of carbon fixation should have used some of the key organic compounds that participate in central anabolism today. The prebiotic system should have implemented the core reactions involved in central metabolism abiotically and nonezymatically [2]. The model is based on sulfur-containing semiconductor minerals, in situ produced in a shallow sea hydrothermal vent [3]. The advantage of the model is to use free energy from sunlight photons to drive otherwise unviable reactions in the absence of enzymes using photocatalysts.

Current work examines the origin of metabolism in a simulated prebiotic shallow water hydrothermal vent. Zinc sulfide (ZnS, sphalerite) was used as a candidate mineral to jumpstart the origin of metabolism in chemoautotrophs. Photochemical reactions of simple organic compounds with carbon dioxide occur at the semiconductor interface. The experimental results show the production of C2, C3, C4, C5, and C6, intermediates of central metabolism [4]. Starting from CO2, and by consecutive reactions, we observed formate, acetate, oxalate, glyoxylate, glycolate, lactate, pyruvate, succinate, α-ketoglutarate, and isocitrate. The mechanism provides a way to capture energy from the environment while producing carbon feedstock useful in anabolism. The results of this study suggest that central metabolites could have participated in a viable enzyme-free cycle for carbon fixation in a shallow sea hydrothermal vent, where light, sulfide minerals, carbon dioxide, and other organic compounds interacted on the prebiotic Earth to generate an autonomous chemical cycle [5].

Melt inclusions in coexisting perovskite, nepheline, magnetite and clinopyroxene in pyroxene melilitolite from Kerimasi Volcano, Tanzania

T. GUZMICS1*, R.H. MITCHELL2, M. BERKESI1, C. SZABO1 AND R. MILKE3

1Lithosphere Fluid Research Lab, Institute of Geography and Earth Sciences, Eötvös University Budapest, 1117 Pázmány Péter sétány 1/C, Budapest, Hungary (correspondence: tibor.guzmics@gmail.com)
2Lakehead University, Thunder Bay, ON P7B 5E1, Canada
3Free University, Habelschwerdter Allee 45, 14195 Berlin, Germany

We studied melt inclusions in pyroxene melilitolite from Kerimasi volcano, Tanzania. Primary silicate melt and fluid inclusions were entrapped in perovskite, magnetite, nepheline and clinopyroxene, however, perovskite usually enclosed multiphase melt inclusions containing both silicate and carbonatite melt (Fig. 1).

Figure 1: Quenched melt inclusions containing immiscible melts in perovskite after heating to 1050 °C.

High temperature heating experiments on melt inclusions show minimum homogenization temperatures at 1040 °C in clinopyroxene and at 1050 °C in nepheline and perovskite, which correspond to actual crystallization temperature. Nevertheless, in many cases, heterogeneous entrapment of melts and fluid prevented complete homogenization of melt inclusions. We applied furnace technique in order to produce homogenous melt(s). Melt compositions indicate an earlier formation of this rock than Kerimasi calcicocarbonatite.

CO₂ sequestration and hydrothermal basalt alteration at 40-250 °C

A. P. GYSI* AND A. STEFÁNSSON

Institute of Earth Sciences, University of Iceland, 101 Reykjavik, Iceland (*correspondence: apg2@hi.is)

In order to gain insight into the geochemical processes associated with CO₂ mineralization and sequestration in basalts, a series of CO₂-water-basaltic glass reaction path experiments and numerical simulations were performed at 40-250 °C and initial pCO₂ of 0-20 bar, and the water chemistry and the secondary minerals studied as a function of reaction progress.

At 40-75 °C, the addition of CO₂ changes the water-basalt reaction path considerably. At low reaction progress (pH <6.5), the pH was buffered by CO₂ ionization, consumption of protons (H⁺) by the dissolving basaltic glass and proton consumption-release upon secondary mineral formation. The stable mineralogy consisted of Ca-(Mg)-Fe clays, amorphous SiO₂ and Ca-(Mg)-(Fe)-carbonate (ankerite) solid solutions. The moles of carbonates and SiO₂ per moles dissolved basaltic glass was observed to increase at elevated pCO₂, whereas the amount of clays forming decreased. At high reaction progress (pH >8), the pH was buffered by the basalt alteration and secondary mineral formation and dissolved silica ionization. The stable mineral assemblages consisted of Mg-Fe clays, zeolites and Ca-Mg carbonates.

At 150-250 °C, the secondary mineral assemblages formed during the experiments where similar to those observed in natural geothermally altered basalts, and consisted of amorphous SiO₂, mixed Mg-Fe smectites/chlorite, zeolites and calcite. The amount of clays and a basaltic glass surface alteration layer increased in thickness with temperature, coating sometimes the entire basaltic glass surface. At 250 °C, the clay compositions were generally closer to chlorite and the basaltic glass completely altered after ~50 days, whereas at 150 °C a thin alteration layer was observed after ~125 days reaction time.

The dissolution of basaltic glass in CO₂-rich waters was found to be incongruent with the overall water composition and secondary mineralogy depending on pH, reaction progress and temperature. Competing reactions between clays (Ca-Fe smectites) and carbonates at low pH, and zeolites and clays (Mg-Fe smectites) and carbonates at high pH, control together the availability of Ca, Mg and Fe, playing a key role for CO₂ mineralization and sequestration into basalts [1, 2].